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A STUDY OF ALLOY SURFACES USING
LOW ENERGY ELECTRON DIFFRACTION
AND AUGER ELECTRON SPECTROSCOPY

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ABSTRACT

Low Energy Electron Diffraction and Auger Electron Spectroscopy have been applied to very simple alloy situations in which calibrated films of copper and gold have been grown epitaxially on platinum single crystals. The results of the quantitative use of A.E.S. for these alloy systems were found to depend on the presence of impurities and the surface atom geometry. LMM Auger peaks from copper films of >3 monolayers on Pt(100) were enhanced after oxygen treatment while no peak shape changes were detected.

Low surface mobility of copper on Pt(100) at 20°C prevented complete monolayer growth with apparent mean free paths for 927 eV and 239 eV electrons in copper of 3.13 ± 0.47 and 2.40 ± 0.36 monolayers at the copper density of 1.54×10^{19} atoms m^{-2} /monolayer. True monolayer growth occurred after 2 monolayers when the 927 eV m.f.p. was found to be 1.91 monolayers ($3.45 \pm 0.52 \text{ \AA}$).

Pseudomorphic growth of copper on Pt(100) was observed up to 6 monolayers (platinum surface density 1.30×10^{19} atoms m^{-2} /monolayer) at 20°C. Gas adsorption on these surfaces differed from that on Pt(100) and did not form all reported Cu(100) structures. The adsorption of H_2S , followed by LEED and A.E.S., enabled copper island areas to be determined in films of <2 monolayers.

Copper formed disordered arrangements on Pt(111) at 20°C but grew epitaxially at 400°C.

A Pt(100) crystal surface exhibited a Pt(100)-(5x1) LEED

pattern when cleaned to show no impurities by A.E.S. or when carbon was detected by LEED and A.E.S. The Pt(100)-(5x1) pattern, attributed to incomplete layers of distorted Pt(111) on Pt(100), reverted to Pt(100)-(1x1) after deposition of $<0.1 \text{ \AA}$ of copper or gold.

Gold formed a Pt(100)-(7x1)-Au structure after 4.5 monolayers. This was attributed to a distorted Au(111) surface layer.

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This thesis has been typed by my wife [REDACTED].

CHAPTER I INTRODUCTION

I.1 Surface Studies

Molecular collisions with surfaces are the fundamental acts in the processes of catalysis, lubrication and corrosion, the commercial importance of which has encouraged the study of interactions at surfaces using every technique available. Surfaces may only be cleaned and closely specified if maintained in an Ultra High Vacuum (U.H.V.) environment to reduce the rate of surface contamination. However, the use of electron beams and similar probes in such an environment may cause degradation of the surface to be studied, invalidating the results of the study.

An important technique in the study of surfaces of catalytic importance is Low Energy Electron Diffraction (LEED). This has been used to attempt to explain the operation of heterogeneous catalysts by several groups, notably Edmonds, McCarroll and Pitkethly⁽¹⁻¹⁰⁾ who produced and analysed surface structures on nickel, and Somorjai et al⁽¹¹⁻²²⁾ who have studied absorption of many gases on platinum. The restraints set by this technique, using a single crystal $\sim 1\text{mm}$ across in U.H.V., mean that correlation with a commercial catalyst with $50\text{\AA}$ metal crystallites operating in gas pressures of several atmospheres may appear tenuous but has been shown to be very relevant by McCarroll, Edmonds and Pitkethly⁽¹⁾. The electron beam is of sufficiently low energy to cause little modification to the surface by cracking or desorption except of very weakly held

adsorbates⁽³⁾.

The information obtained from LEED gives only the two dimensional periodicity of the crystal surfaces but should soon enable surface structures to be determined when a general method of analysis is developed.

In many studies, where the LEED pattern resulting from a cleaning treatment or gas adsorption may not be simply explained, a surface analysis must be carried out. The most sensitive technique for all elements except hydrogen is Auger Electron Spectroscopy (A.E.S.). By using the vacuum components of the LEED apparatus for A.E.S. the two techniques are complementary, providing surface geometry and elemental analysis information.

An area of expanding interest in catalyst development is that of alloy catalysts. Alloys may improve catalyst performance and reduce the quantities of expensive metals used in their production. The bulk properties of alloys have been studied extensively but the surfaces are less well known.

A.E.S. is the ideal method for studying surfaces where the concentration of components may differ from that of the bulk. However, the spectra obtained from surfaces may not be used quantitatively until absolute or comparative studies have been carried out for yield and absorption of Auger electrons in all elements detected.

The work described here is the deposition of metal films, particularly copper, on platinum single crystals. Platinum has been studied extensively by many techniques

to try to understand its operation as a catalyst. A controversy has arisen over the apparently clean surface of the Pt(100) crystal which exhibits a LEED pattern which is not simply related to the (100) plane in the bulk of the crystal. Gold and iridium also exhibit a similar non-bulk (100) pattern which probably has the same cause in all three metals. As Palmberg has proposed that the surfaces have reorientated from (100) to (111) an understanding of the cause is a vital link in the action of platinum as a catalyst for reactions where a 'key' fit occurs between the gas phase species onto the metal surface. Copper has been the subject of high resolution A.E.S. and is well documented in LEED studies.

The combination of the LEED and A.E.S. techniques used by Palmberg in his initial calibration of the sampling depth of A.E.S. had not been commonly applied to the growth of metal films at the start of this work but several reports have since been published. These methods are effective in monitoring the growth of metal films deposited on various substrates when LEED may be used to determine the atomic spacing, orientation and presence of epitaxy in the film. The growth of the A.E.S. signal due to the film and decrease of that from the substrate indicates the growth process of the film. The limit of pseudomorphic growth may be determined if the surface film is calibrated during deposition and removed by etching.

The operation of a metal surface as a catalyst depends on the surface atomic structure/geometry and electronic

properties. The occurrence of pseudomorphic growth enables the relative importance of these factors in adsorption and subsequent catalysis to be assessed.

I.2 Methods Employed

I.2.1 Vacuum Requirements

The development of surface sensitive techniques has been closely related to the ability to clean the surface of interest and to treat the surface with sufficiently high purity materials at a low rate to enable changes to be observed. The most generous limit of the Ultra High Vacuum (U.H.V.) environment is taken as 10^{-8} torr ($1.3 \mu\text{N m}^{-2}$) but at this pressure of nitrogen at room temperature a clean surface with a unity sticking factor for nitrogen would be covered with a monolayer in about 2 mins. A pressure of active gas reduced by a factor of 10^{-2} from this gives an adequate working time for many experiments.

Conversely, the difficulty in obtaining U.H.V. conditions may be understood from the long period during which a single monolayer of adsorbed gas on the vacuum system walls will maintain the system pressure during desorption despite the use of high pumping rates. Even with low surface coverages the number of molecules on the system walls is several orders of magnitude higher than that in the gas phase. The methods used to obtain U.H.V. conditions routinely are now standard technology. A useful review of the

field of surface studies in U.H.V. is given by Hobson⁽²³⁾ (100 refs). Even this review paper, published in 1974, refers exclusively to pressures in torr and not the S.I. units of N m^{-2}

$$\text{where } 1 \text{ torr} \equiv 133 \text{ N m}^{-2}$$

I.2.2 The Energy Distribution of Electrons from Surfaces.

Electrons leaving a surface irradiated by an electron beam carry information about the surface. The energy distribution is generally of the form shown in Figure I.1 with 3 regions of interest.

- A) The elastic peak at the primary beam energy, ' E_p ', with associated loss peaks.
- B) The relatively flat intermediate energy region of the curve in which very small peaks due to Auger electrons may be seen.
- C) A large broad peak in the range 0-100eV.

Fine structure peaks in the spectra are of two types, dependent or independent of primary beam energy. The Auger and true secondary electrons are of the latter type and so may be distinguished from the former type by a change in exciting beam energy. The elastic peak follows the beam energy and may have several loss peaks regularly spaced in energy below it.

Region A The Elastic Peak

Electrons from the exciting beam which are reflected from the surface with no loss in energy make up the highest energy peak of the distribution. These electrons have an angular distribution dependent on the surface crystallography

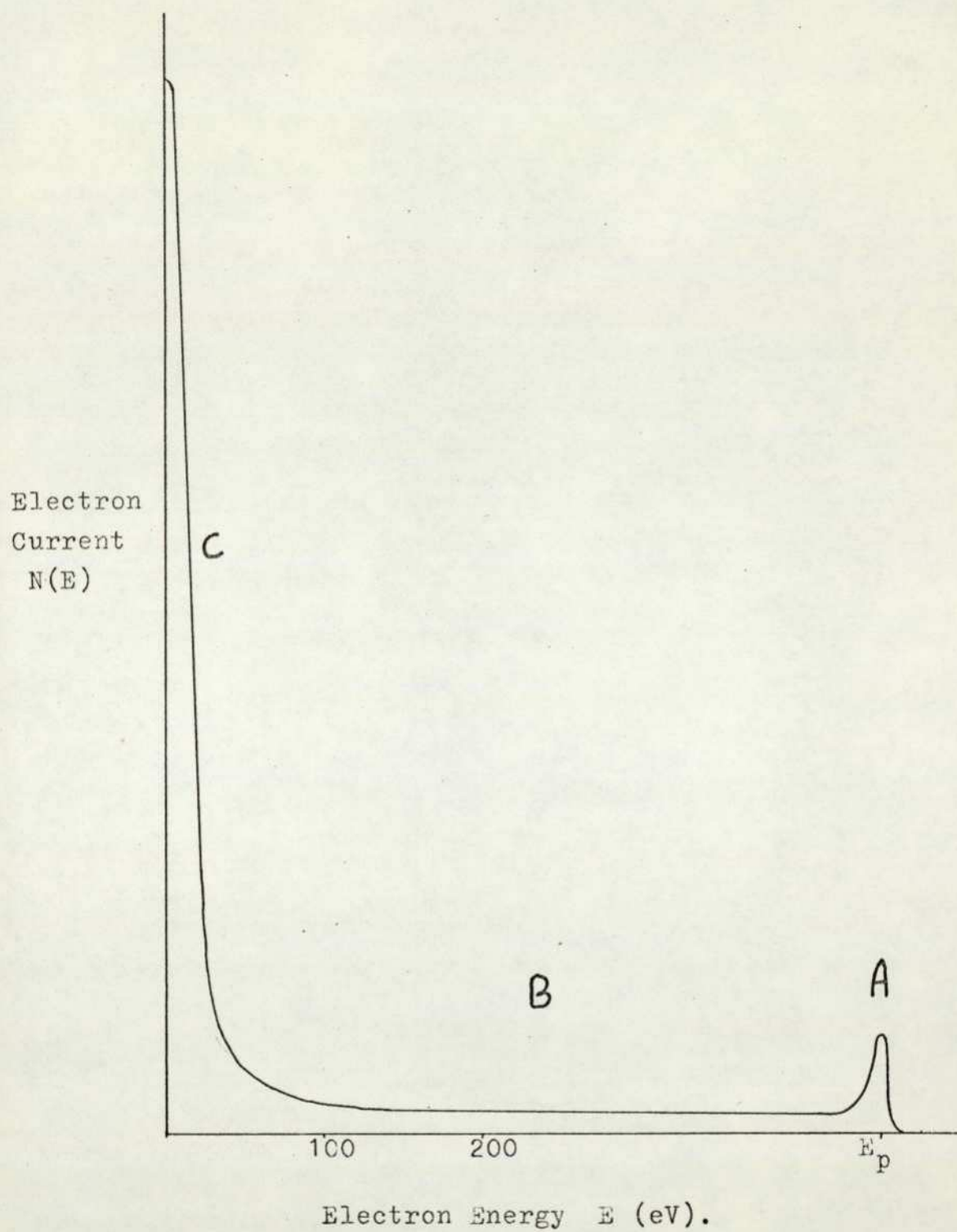


FIGURE I.1

The secondary electron energy distribution. No fine structure is shown.

as illustrated in LEED. In this peak it is not usually possible to resolve the electrons which have lost a small amount of energy in phonon interactions.

Some of the electrons which would contribute to the elastic peak lose energy by setting up a plasma oscillation in the solid and so lose one or more units of plasmon energy. These 'plasmon loss' electrons appear as satellite peaks below the elastic peak with a separation depending on the free electron nature of the material. Similarly these satellite peaks may appear below strong Auger electron peaks.

Region B

The middle region is made up of a relatively smooth distribution of secondary electrons. The Auger electron peaks, which appear throughout the distribution, are seen most clearly in this section although they are only a small proportion of the background current. The method of electronic differentiation introduced by Harris enables this background to be suppressed and so allows sufficient amplification to be used to display the differentiated Auger peaks clearly.

Ionization loss effects may also be seen in this region. The incoming electron may ionize an atom by removing a core electron; the two electrons then have a total energy of $(E_p - E_B)$ where E_B is the binding energy of the core electron. The maximum energy of this distribution occurs when one electron remains at the Fermi level in the material, i.e. zero energy, and the other escapes with energy $(E_p - E_B)$. This cut-off may be sufficiently sharp to be observed but may

be distinguished from Auger effects by a change in beam energy.

Region C The Slow Peak

During electron bombardment most electrons from the sample are in this low energy range and result from cascade interactions with valence electrons after which a proportion still have sufficient energy and are travelling in a suitable direction to escape. These electrons have suffered so many interactions that the incoming electron energy is totally masked.

I.2.3 Low Energy Electron Diffraction

I.2.3.1 Introduction

Diffraction of electrons by crystal surfaces is the striking proof of the wave nature of electrons as proposed by de Broglie⁽²⁴⁾ in 1924. The diffraction patterns due to low energy electrons are largely characterised by the geometry of the outer atomic layer of the crystal and may be used to gauge surface meshes. The electrons entering the crystal interact strongly with the surface atoms and are unlikely to penetrate further than the first few monolayers. The strong interaction may cause an electron to undergo multiple scattering events before escaping from the crystal.

The strong interaction makes the theory used for X-ray diffraction, with its low interaction, only partially applicable. The theories and experimental conditions applied to LEED presently have been reviewed by Owens⁽²⁵⁾ and

Prutton⁽²⁶⁾. An extensive series of detailed discussions has been published as the proceedings of a Summer School on LEED methods in Czechoslovakia in 1971⁽²⁷⁾. The theories described here are those used to analyse the patterns observed in this work.

I.2.3.2 Surface Mesh Conventions

The surface mesh conventions have been standardised after the paper by Wood⁽²⁸⁾. The three lowest index planes of f.c.c. metals, with square, hexagonal and rectangular meshes are drawn in Figure I.2 with the other two possible unit meshes shown also.

The reciprocal mesh is related to the real mesh by

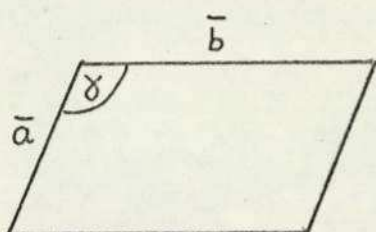
$$\begin{aligned}\vec{a} \cdot \vec{a}^* &= 1 = \vec{b} \cdot \vec{b}^* \\ \vec{a}^* \cdot \vec{b} &= 0 = \vec{b}^* \cdot \vec{a}\end{aligned}$$

where $\vec{a}$ and $\vec{b}$ are the vectors representing the sides of the real unit mesh while $\vec{a}^*$ and $\vec{b}^*$ are the reciprocal mesh vectors.

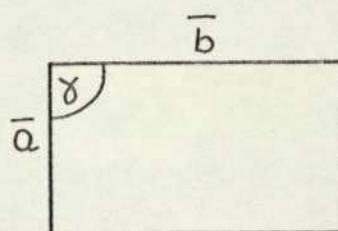
The description of these vectors in matrix form, described by Park and Madden⁽²⁹⁾, makes manipulation of complex meshes a standard procedure.

I.2.3.3 LEED Theories

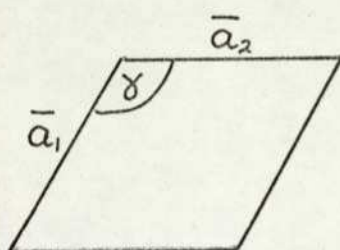
The simplest, kinematic, approach (Buerger⁽³⁰⁾) describes the waves emanating from a 1, 2 or 3 dimensional array of scattering centres after excitation by an incident electron beam. The Huygens' wavelet construction produces a series of cones for each direction in the lattice. Diffracted beams then occur in the few directions along which cones from each of the three directions intersect for an incident



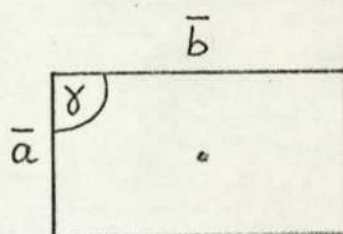
Oblique
 $a < b$
 $\gamma > 90^\circ$



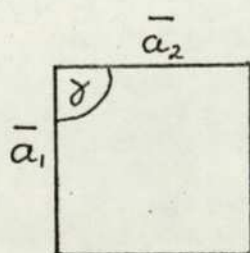
Rectangular
 $a < b$
 $\gamma = 90^\circ$



Hexagonal
 $a_1 = a_2$
 $\gamma = 120^\circ$



Centred Rectangle
 $a < b$
 $\gamma = 90^\circ$



Square
 $a_1 = a_2$
 $\gamma = 90^\circ$

FIGURE I.2 The 5 basic unit meshes.

beam penetrating many layers from the surface, or the less demanding situation of diffraction solely by the surface mesh from which more beams may occur. The diffraction cone description is formalised in the Laue equations which must each be satisfied for diffraction to occur.

This solution occurs when the Ewald's sphere, of diameter the wavelength of the electron beam, crosses a reciprocal lattice rod for diffraction from a surface mesh, or point for a lattice. Both 2 and 3 dimension effects must be considered for LEED; the reciprocal mesh rods are modulated by diffraction from inner planes in the crystal. Any energy spread or divergence in the incident electron beam thickens and distorts the Ewald's sphere making the area of cut with the rods greater, i.e. broader diffracted beams.

The kinematic theory predicts that the scattered beams from a surface irradiated at normal incidence follow the expression:-

$$n\lambda = d_{hk} \sin \Theta$$

where λ is the electron wavelength

Θ is the angle between incident and diffracted beams

d_{hk} is inter _{λ} row spacing of the surface atoms

n is the (integer) order of diffraction.

The electron wavelength is given by the de Broglie expression:-

$$\lambda = h/p \div \sqrt{150/V} \text{ \AA}$$

where V is the electron accelerating field in volts

h is Planck's constant

p is the electron's momentum.

The condition for which the Ewald's sphere is contracted so as not to cross any reciprocal lattice rods occurs as $n\lambda/d$ exceeds 1 when $\sin \theta$ is indeterminate, i.e. the 1st order patterns will always be present when the electron wavelength is less than the interrow spacing. This condition of cut-off may be used as a test of simple single scattering events.

As penetration beyond the surface layer is considered the Bragg lattice reflection modulation will follow the form

$$n\lambda = d_z(1 + \cos \phi)$$

where d_z is the interplanar spacing perpendicular to the planes.

The inadequacy of the kinematic model^{is} shown in a plot of diffracted spot intensity (I) against incident beam energy (V) at constant beam current. A solely surface mesh diffraction would result in constant intensity beam; with additional atomic layers the beams would be modulated to give Bragg-type interlayer reflections. The increasing proportion of electrons from the incident beam lost in inelastic processes as the electron beam energy is raised and penetration increases causes a reduction in diffracted beam intensity. However, additional variations are observed in the $I(V)$ curve; a considerable number of theoretical studies is being carried out to explain these effects. The information in the $I(V)$ curve should reveal the detailed structure of the irradiated surface when a general method

is developed.

The spot intensity varies with several parameters as described by Owens⁽²⁵⁾. The $I(hk)$ description refers to the constant beam energy diffraction pattern from which the surface mesh is obtained. The errors of photographing the apparently straight lines on a curved screen have been discussed by Taylor⁽³¹⁾ and Lyon⁽³²⁾ but are minimal if similar patterns are compared under identical conditions. Absolute measurement of surface mesh dimensions requires close tolerance experimental conditions.

The fitting of the $I(V)$ curve holds most structural information. The components of the surface mesh must be separately assessed for their interaction (i.e. atomic scattering factor with wavelength and angle dependence) with the incident electron beam and the effects summed over the unit mesh.

Lander⁽³³⁾ modified the structure factor to allow for screening of the inner layers to the incident beam. The absorption by each layer is large, with an atomic cross section for electrons below 100 eV similar to the atom area.

McRae⁽³⁴⁾ developed a self consistent multiple scattering theory based on a "muffin tin" abrupt edged potential description. He summed the effects on each atom of the incident electron wave field and the emitted field of surrounding atoms. The resultant wave emissions from the surface atoms are both propagating and non-propagating or evanescent. This model explained fractional order peaks as interference between different/propagating waves in the

field in the crystal surface. The special case of the incident beam wavelength matching a surface periodicity is explained as a surface resonance in this model.

Boudreaux and Heine⁽³⁵⁾ have described strong reflections as being due to the electron energy matching the band gap in the surface material. The wave field is largely determined by the surface layer properties.

The decrease of cross section for both elastic and inelastic collisions with increasing incident beam energy makes the kinematic approximation accurate at a high energy (typically 200 eV) but Xe(111) has been shown to follow this model over most of the low energy range by Ignatjevs, Pendry and Rhodin⁽³⁶⁾.

In calculations ignoring the effects of inelastic scattering the predicted peak widths in the $I(V)$ curve are considerably narrower than experimentally observed widths. Inelastic scattering removes electrons which may have contributed to multiple scattering events. By including this effect Duke and Tucker⁽³⁷⁾ fitted spectra with accurate peak widths.

Reid's⁽³⁸⁾ study of the $I(V)$ curve shape for Cu(100) at different temperatures has shown that the crystal temperature influenced the relative heights of some peaks; temperature effects obviously are necessary in any calculations. These results also show the importance of accurate measurement of beam angle of incidence as the curve shapes changed considerably over a few degrees.

For face centred cubic metals with surfaces which

correspond to an undistorted truncation of the bulk, Jepsen, Marcus and Jona⁽³⁹⁾ have fitted aluminium and copper I(V) curves well with a model including a band structured ion core-electron interaction, inelastic scattering, surface vibration temperature effects and the inner potential correction from an empirical fit with experiment. This theory is less accurate at increasing angle of incidence when the geometry and scattering properties of the outer atoms are less accurately predicted.

The microscopic-model method is based on a trial and error manipulation of surface atoms with a multiple scattering calculation with theoretical scattering factors for each arrangement. Andersson and Pendry⁽⁴⁰⁾ have studied monolayer growth of sodium on nickel and found best agreement with Na atoms 0.29 nm above the Ni surface in the four fold symmetry gaps of the surface atom arrangement. This proposed spacing has been recently modified in an improvement in their theory. The method has been more successful for the 00 beam than higher order.

To avoid the complications of the dynamic theory the fine structure in the I(V) curve may be lost in an averaging technique. The reduced curve may then be analysed with a kinematic method. This has been applied to the beams due to adsorbed monolayers by Tucker and Duke⁽⁴¹⁾. Lagally, Ngoc, and Webb⁽⁴²⁾ have produced a simple averaged curve for silver which exhibits largely kinematic features. When the data can be reduced so that I(V) curves exhibit solely kinematic effects standard X-ray analysis methods may be

used to determine surface structure.

I.2.3.4 The $I(T)$ Plot

The spot intensity variation with temperature gives a measure of the thermal movement experienced by the surface atoms using the Debye Waller relationship. Estrup⁽⁴³⁾ proposed that if a standard curve can be recorded for a specified surface, any deviation from this plot for an identical $I(hk)$ pattern reveals a changed surface.

I.2.3.5 The $I(\theta)$ Plot

The coverage (θ) of a surface so as to produce new diffraction spots may be followed if the intensity of a new spot is recorded. This is valid only if constant emission from the gun can be maintained during gas adsorption.

I.2.3.6 LEED from Real Surfaces

The theoretical assumptions of atomically smooth uncontaminated surfaces are not obtainable in practice but the LEED pattern is not rapidly degraded by surface imperfections as gross as those due to extensive argon ion bombarding (Park⁽⁴⁴⁾). However the $I(V)$ curve is more variable with both surface ^{im}perfections and presence of impurities (Park and Farnsworth⁽⁴⁵⁾).

The experimental use of LEED is to determine the surface characteristics and follow changes in geometry and surface species using the LEED pattern and/or spot intensity monitoring.

In alloying studies the LEED pattern changes with order-disorder effects have been described by Lander⁽³³⁾ and also Estrup and Anderson⁽⁴⁶⁾ who

described one dimensional "thin film growth". They found that an island structure of good order within the islands produced sharp additional spots while random vacancies in a well ordered film produced sharp spots on a raised background. Short range ordered films gave a very diffuse level for the additional diffracted spots. Such analysis is useful in the analysis of thin film growth in a LEED system. Island growth was shown to cause intermediate pattern streaking by Tracey and Blakely⁽⁴⁷⁾.

I.2.3.7 Surface Structures

A simple LEED pattern may be easily related to the surface periodicity. Where different orientations are possible the relatively large electron beam size will excite regions with all domains. Where adsorption of a light gas on a metal crystal results in a strong change in pattern it is probable that the gas has caused a reconstruction of the metal surface as the different beams from adsorbed species alone will be small.

Bauer⁽⁴⁸⁾ proposes that reconstruction may occur when the bonding strength is similar for surface atoms to the bulk and adatoms to the surface.

Ordering of thin films into surface alloys is a reconstruction process and shows as additional satellite spots around the substrate spots.

I.2.3.8 Multiple Scattering

Bauer⁽⁴⁹⁾ suggests a multi-scattering approach for complex patterns where the diffracted beams from the substrate are diffracted a second time by the adsorbate with little loss

of intensity due to the forward scatter process.

The diffraction from a super-lattice in which the overlayer spacing is an integer number of substrate mesh inter-row spacings is similar to a coincidence mesh in which an integer number of overlayer spacings coincides with a different integer number of substrate spacings. Tucker⁽⁵⁰⁾ showed that only the superlattice could maintain diffraction conditions at very low voltages when the multiple diffraction effects in the coincidence lattice were not possible as $\lambda/d > 1$ (see Section I.2.3.3). This distinction was questioned by Jona, Lever and Gunn⁽⁵¹⁾; the cut-off occurs for propagating waves only but the evanescent surface waves may give rise to propagating waves if an adsorbate mesh is sufficiently near to the substrate to give significant beams. The condition that all meshes are below the cut-off spacing for multiple scattering is relaxed to the last mesh causing scattering being below the cut-off.

Multiple scattering is considered in the discussion of the Pt/Au/Ir(100) surface structure in Section I.3.1.

I.2.3.9 LEED Experimental Considerations

In the original LEED experiments by Davisson and Germer⁽⁵²⁾ a Faraday cup was used to measure the secondary current angular distribution and this method has been used recently for accurate measurements by Seah⁽⁵³⁾ and Park and Farnsworth⁽⁵⁴⁾. The complex accurate cup movements^{needed} within a vacuum system have encouraged the use of fluorescent display systems developed from the plane grid system of Scheibner, Germer and Hartmann⁽⁵⁵⁾. The energy selection

of the plane grids depends on the angle of incidence of the electrons, resulting in a decrease of background and loss of diffraction pattern with increasing distance from the screen normal through the crystal.

The magnetic deflection system developed by Tucker⁽⁵⁰⁾ results in a distorted pattern but enables a complete pattern of all back diffraction from the surface to be viewed without the obstruction of the direct reflection (0,0) spot.

The most commonly used LEED method is that of Lander, Unterwald and Morrison⁽⁵⁶⁾ using a spherical grid system with the crystal face at the centre of curvature of the grids and screen. When run in a field free mode the diffracted 'cones' cut the screen in a line which appears straight when viewed perpendicularly to the front face of the grid structure.

The crystal, chamber walls and front grid are earthed to maintain an electrical field free region through which the secondary electrons drift unchanged in direction if magnetic fields are eliminated. The next grid approached by the electrons after passage through the front grid is maintained at the electron gun filament potential. Any electrons which have lost energy since leaving the gun are repelled while the elastically scattered electrons pass through to be accelerated to a high potential, phosphor coated, screen. With this two grid system, field penetration from the screen-inner grid region may degrade the elastic/inelastic cut-off and distort the diffracted beams, although the use of a third grid also held at filament potential

to reduce field penetration will reduce transmission and may introduce Moire fringes. However the importance of 3 and 4 grid "optics" in Auger Electron Spectroscopy studies has increased their usage. The construction of LEED optics and guns in UHV systems is now technically routine and complete systems may be purchased from several manufacturers.

I.2.3.10 Gas Adsorption on Platinum Crystals

Gas adsorption on platinum surfaces has been studied by many workers. The results are summarised in the following tables.

Pt(100)

Gas	Structure	Ref./Date	Notes
Oxygen	(1x1)	32/1967	20°C (due to CO)
	(5x1)	"	400°C
	(5x1)	11/1968	20°C
	(2√2x√2)	"	annealed in oxygen, due to C or CO
	(5x1)	57/1972	
Hydrogen	(2x2)	11/1968	High Hydrogen
		58/1972	pressure
	(2x2)	59/1970	
Carbon	(4x2)	60/1964	20°C, 1 x 10 ⁻⁶ torr
Monoxide	(3√2x√2)	"	>80° or electron beam
	(1x1)	32/1967	From Background
	(√2x√2)	"	20°C 2000 L
	(4x2)	11/1968	<130°C Reversible, but
	(1x1)	"	300-600°C graphite ring
	(√5x√5)	58,16/1972	forms
	(√2x√2)	"	
Carbon Dioxide	(5x1)	11/1968	
Methane	(5x1)	11/1968	
Ethyne	(√2x√2)	11/1968	<150°C

Ethyne	$(\sqrt{2} \times \sqrt{2})$	16,58/1972	20°C
Ethene	$(\sqrt{2} \times \sqrt{2})$	61/1972	
	$(\sqrt{2} \times \sqrt{2})$	16,58/1972	
Ethane	(5x1)	11/1968	Graphite ring observed
Propene	(1x1)	16,58/1972	
2-Butene (cis)	(1x1)	16,58/1972	
2-Butene (trans)	(1x1)	16,58/1972	
1-3 Buta- diene	(1x1)	16,58/1972	
2 Methyl Propene	(1x1)	16,58/1972	
Naphtha- lene	(1x1) Disordered	16,58/1972 17/1973	
Pyridine	$(\sqrt{2} \times \sqrt{2})$ (1x1) $(\sqrt{2} \times \sqrt{2})$	16,58/1972 17/1973 "	20°C >250°C
Pyrrole	$(\sqrt{2} \times \sqrt{2})$	16,58/1972	
Benzene	(1x1) (2x2)	17/1973 "	disordered
Carbon	Ring	11/1968	from hydrocarbons

Hydrogen	(2x2)	62/1971	low exposure
Sulphide	($\sqrt{2} \times \sqrt{2}$)	"	higher exposure
	(2x2)+(5x1)	"	20°C
	(2x2)	"	increasing exposure
	($\sqrt{2} \times \sqrt{2}$)		" "
Nitrogen	(5x1)	11/1968	
Nitrous Oxide	(5x1)	11/1968	
Pt(110)			
Oxygen	(1x1)	32/1967	
Hydrogen	(1x1)	32/1967	
Carbon Monoxide	(1x1)	32/1967	
Hydrogen	c(2x6)	63/1973	$6-16 \times 10^{-9} \text{ gm/cm}^2$
Sulphide	complex	"	$16-20 \times 10^{-9} \text{ gm/cm}^2$
	p(2x3)	"	$20-30 \times 10^{-9} \text{ gm/cm}^2$
	p(4x3)	"	$30-33 \times 10^{-9} \text{ gm/cm}^2$
	c(2x4)	"	$33-37 \times 10^{-9} \text{ gm/cm}^2$
	p(4x4)	"	$37-38 \times 10^{-9} \text{ gm/cm}^2$
Pt(111)			
Oxygen	(2x2)	32/1967	Carbon?
	(1x1)	64/1971	
	(2x2)	65/1973	No C by A.E.S.

Hydrogen	(2x2)	58/1972	
Carbon	c(4x2)	58/1972	
Monoxide	(2x2)	"	
	(1x1)	66/1973	diffuse
Hydrogen + Carbon Monoxide	($\sqrt{3} \times \sqrt{3}$)	58/1972	
Ethyne	(2x2)	16,58/1972	
Ethene	(2x2)	67/1970	<200°C
	(2x2)	16,58/1972	
Butene	(2x2)	16,58/1972	
1-3 Buta- diene	(2x2)	16,58/1972	
2 Methyl Propene	($\sqrt{7} \times \sqrt{3}$)	16,58/1972	
Naphtha- lene	(3x3)	16,58/1972	<150°C
	(6x6)	"	>150°C
Pyrrole	(4x2)	16,58/1972	
	(4x4)	"	
Pyridine	(3x1)	16,58/1972	
	(2x2)	17/1973	<250°C low pressure
	(3x3)	"	>250°C

Benzene	(2 $\sqrt{3}$ x4)	17/1973	<100°C
	(2 $\sqrt{3}$ x5)	"	>100°C
Carbon	(2x2)	64/1971	Stable above 1000°C
	Ring	16,58/1972	Graphite
Hydrogen	(2x2)	62/1971	
Sulphide	($\sqrt{3}$ x $\sqrt{3}$)	"	increased exposure

Clean Surface Structures Reported for Platinum

Pt(100)

Pattern	Reference	Notes
(5x1)	14/1965	
(5x1)	32/1967	Alumina abrasives, aqua regia etch
(5x1)	15/1967	Stable to 500°C
(2x1)	"	300-500°C
Ring(Graphite)	"	>700°C
(5x1)	11/1968	
(1x1)	68/1969	Oxygen on hot crystal
(5x1)	16/1972	
(5x1)	63/1973	
(5x1)	69/1973	Model proposed assumed no impurity.
(5x1)	17/1973	No contamination detected by A.E.S.
<u>Pt(110)</u>		
(2x1)	32/1967	700 L of oxygen at 1200°C
(3x1)	"	Annealed at 1380°C
(4x1)	"	" " "
Ring	15/1967	Graphite, annealed at 600°C

(1x3)	63/1973	No impurities by A.E.S.
(1x2)	"	Carbon detected by A.E.S.
Pt(111)		
(2x2)	15/1967	800-1000°C
(3x3)	"	"
Ring	"	>900°C
(1x1)	67/1970	Polished, etched, ion bombarded, annealed
(1x1)	64/1971	
(1x1)	70/1971	
(1x1)	17/1973	

I.2.3.11 Gas Adsorption on Copper Crystal

Cu(100)

Gas	Structure	Ref./Date	Notes
Oxygen	Complex(2x4)	71/1965	Coincidence(5x $\sqrt{13}$)
	(2x4)	72/1967	<450°C
	Complex	"	<500°C
	c(2x2)	73/1967	Facetting 10 ⁻⁴ torr 150°C 30 mins
	c(2x2)	"	20°C 2 hours
	(1.8x1.8)R45°	"	350-550°C Stable to 1000°C
	Hexagonal Oxide	"	>550°C
Nitrous Oxide	(111) Over-layer 1.06a	72/1967	500°C, 6x10 ³ L
	(111) Over-layer $\sqrt{3}a$	"	Pretreat dependent
Nitrogen [N] or N ⁺	None	71/1965	6x10 ⁵ L
	c(2x2)	"	Ionised by electron impact.

Hydrogen	None	71/1965	10^{-4} torr
Carbon	(2x2)	75/1970	$>500^{\circ}\text{C}$
Monoxide	c(2x2)	76/1971	1.4 L 77°K
	($7\sqrt{2}\times 7/5$)	"	Coincidence ($\sqrt{98}\times 10$)
	c(2x2)	77/1971	400 L 20°C
	p(2x2)	"	700-1000 L 20°C
	(1x1)	"	$>100^{\circ}\text{C}$
	c(2x2)	78/1972	0.5 L 77°K
Water	None	79/1967	
Ethene	(2x2)	79/1967	3×10^4 L $<70^{\circ}\text{C}$
Chlorine	(2x2)	80/1972	6×10^2 L 20°C
	c(2x2)	"	6×10^3 L 20°C
Xenon	(111) ring	76/1971	45 L 77°K
Hydrogen	($\sqrt{17}\times\sqrt{17}$)	81/1967	High exposure
Sulphide	(2x1)	82/1971	2×10^{-9} torr 2 L
Cu(110)			
Oxygen	Mix(2x3)	83/1964	10^4 L 800°C
	(3x2), (2x2)	"	
	(1x2)	72/1967	>1 L 5×10^{-8} torr
	(6x2)	"	20°C 6×10^{-4}
	(1x2)	"	350°C
	c(6x2)	73/1967	10^{-4} torr 150°C 30 min
	c(6x2)	84/1969	20°C
	(2x1)	"	400°C 10^{-7} torr

	(5x3)	84/1969	600°C
	Hexagonal 1.57a c(6x2), c(3x1)	74/1972	<450°C
	"	"	>550°C
	Hexagonal 5/√6a	"	>600°C
Hydrogen	(3x3), (2x2)	83/1964	10 ⁴ L 800°C
	(2x3)	"	
Water	(2x1)	79/1967	Reduced O ₂ interaction
Ethene	(2x1)	79/1967	>20 L, <320°C
Carbon	(2x1)	79/1967	20°C
Monoxide	(2x3)	"	250-500°C
Hydrogen Sulphide	c(2x2)	75/1970	10 ⁻⁶ - 10 ⁻⁸ torr, bulk sulphide.
Cu(111)			
Oxygen	Disordered	72/1967	RT
	(7x7), (4x4)	"	300 L 400°C
	(2x2)	"	
	(3x3)	84/1969	7x10 ⁵ L then 350°C
	(√7x√7)	74/1972	} 6x10 ⁻⁴ torr 200-500°C
	($\frac{2}{3}$ x $\frac{2}{3}$)	"	
	(2/2x 2/2)	"	
			>500°C >10 ⁻⁴ torr (Cu ₂ O)
Water	None	79/1967	
Carbon	None	79/1967	20-550°C
Monoxide			

Nitrous Oxide	(2x2)	72/1967	>480°C
Ethene	None	79/1967	6×10^4 L
Hydrogen	($\sqrt{7} \times \sqrt{7}$)	85/1967	20°C
Sulphide	($\sqrt{3} \times \sqrt{3}$)	86/1968	1.5×10^3 L
	($\sqrt{7} \times \sqrt{7}$)	"	

I.2.4 Auger Electron Spectroscopy

I.2.4.1 History of Auger Electron Spectroscopy

Auger Electron spectroscopy (A.E.S.) is a powerful technique for studying surfaces and is being applied to the study of many problems where an analysis of the outer atomic layers is required. The processes occurring have been understood for many years but the application has followed the development of necessary technology in vacuum and electronic methods.

P. Auger⁽⁸⁷⁾, working in 1925, measured the tracks in a Wilson cloud chamber resulting from X-rays of various energies interacting with argon diluted with hydrogen, and realised the significance of pairs of tracks with one track due to constant energy electrons.

Considerable discussion as described by Burhop⁽⁸⁸⁾ followed Auger's paper on the mechanism inside the atom but experimental work was limited. In 1953 Lander⁽⁸⁹⁾ observed small asymmetric peaks on the secondary electron spectra from electron excited metal surfaces, including copper, nickel and platinum, and found carbon as a surface impurity. He observed plasmon loss peaks and suggested the importance of valence band structure in the resulting Auger spectrum.

Further application awaited routine production of a sufficiently good vacuum to enable clean surfaces to be studied, and the use of electronic differentiation of the secondary electron distribution by synchronous detection, introduced by Harris⁽⁹⁰⁻⁹⁸⁾ in 1968. His series of papers covered many surface studies and introduced the technique

through several journals.

The number of laboratories using the technique grew rapidly with papers by Weber and Peria⁽⁹⁹⁾ and Scheibner and Tharp^(100,101) describing how LEED systems could be used for Auger analysis. This was very rapidly developed as many LEED studies could be advanced with knowledge of the surface composition as well as crystal surface periodicity.

Palmberg, Bohn and Tracy⁽¹⁰²⁾ described a cylindrical mirror analyser (C.M.A.) which could be used to give lower noise spectra at high scan rates in systems with or without LEED.

Further developments are being made to improve resolution and sensitivity as the method is applied to a widening field of surface studies. A.E.S. has been reviewed recently by several authors including Rivière⁽¹⁰³⁾ (1969), Dooley and Haas⁽¹⁰⁴⁾ (1970) and Chang⁽¹⁰⁵⁾ (1971).

I.2.4.2 The Auger Process

The processes leading to the ejection of Auger electrons involve three bound electrons of an atom, and occur in two stages. The atom must be irradiated with some form of energy, usually an electron or X-ray beam, which excites an electron from an inner level, ionising the atom. After a short time interval this inner level is filled by a less tightly bound outer electron while a second outer electron is excited by, and carries away, the energy released. This third electron, which has an energy characteristic of its source atom, is detected as the Auger electron.

This process is depicted in Figure I.3. The initial

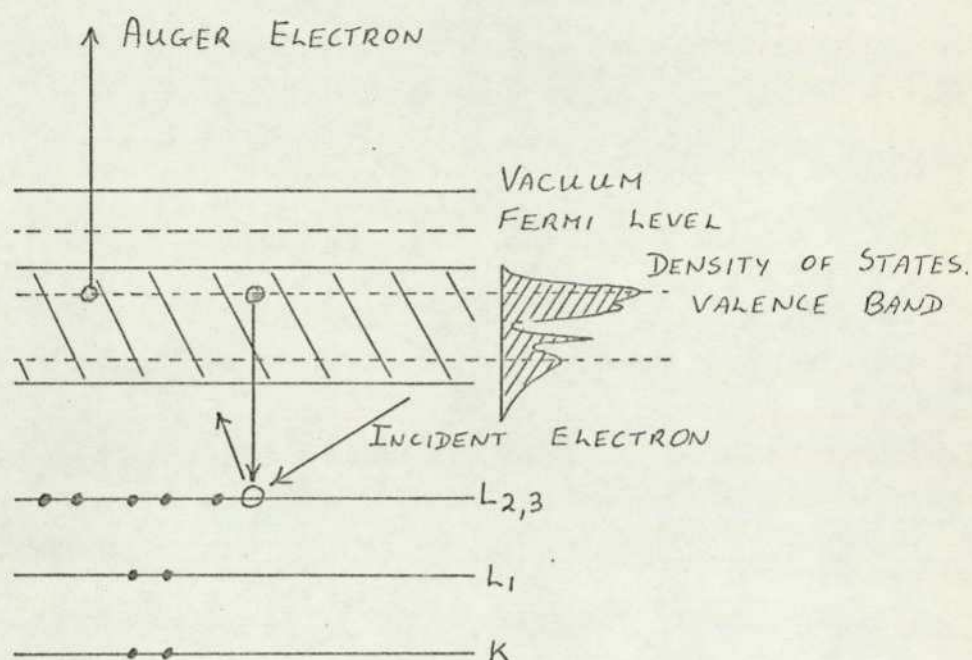


FIGURE I.3 An example of an Auger transition.
Silicon $L_{2,3}VV$.

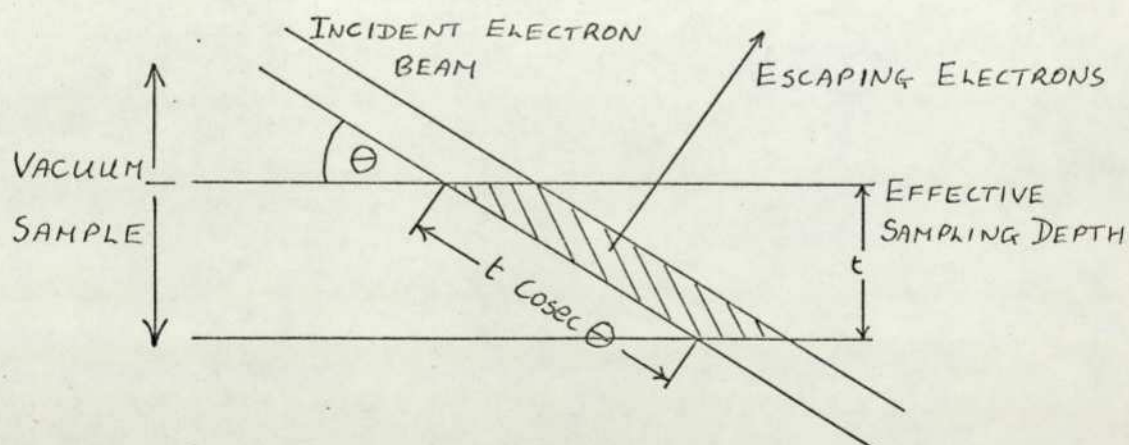


FIGURE I.4 Auger current enhancement at glancing incidence.

ionization occurs in $\sim 10^{-16}$ sec and the lifetime of the resultant state is an order of magnitude greater and so the subsequent processes are not affected by the first.

The original vacancy may also de-excite by fluorescence producing X-ray photons.

Burhop⁽⁸⁸⁾ gives the probability of photon emission(W) in the de-excitation as:-

$$W = (1 + aZ^{-4})^{-1}$$

where Z is the atomic number

$$a = 1.12 \times 10^6 \text{ for K electrons}$$

$$6.4 \times 10^7 \text{ for } L_{III} \text{ electrons}$$

Bishop and Rivière⁽¹⁰⁶⁾ point out that for the range of elements that can be ionised in the K shell and L shell by 2 keV electrons the ionization probabilities are 0.033 and 0.032 respectively. Thus photon production is negligible compared with Auger electron production in this energy range.

After the Auger process has occurred the atom/ion is left in a highly excited state; a chain of fluorescence and further Auger processes may occur until the ion is de-excited.

The nomenclature for Auger processes is of the form 'ABC' where 'A' is the level in which the initial vacancy is formed, 'B' is the original level of the 'down' electron and 'C' is the level from which the emitted electron is ejected. The levels are described with X-ray notation K, L_1 , L_2 , etc.

In solids where the electron levels are broadened the band is labelled and here the Auger energy distribution is related to the density of states in the band.

Moddeman, Carlson, Krause and Pullen⁽¹⁰⁷⁾ have recorded high resolution electron and X-ray excited A.E.S. spectra of common gases. They list possible Auger processes as explanation for the normal and satellite Auger lines. The 'normal' process is defined as one in which a single inner shell vacancy is formed while all other electrons remain in their initial orbitals. The vacancy is then filled by the interaction of two electrons from outer shells to form the final states. In some 20% of cases the formation of an inner shell vacancy unbalances the central potential due to electron shielding and a weakly bound electron escapes either to a higher level or clear of the atom. These processes have been described as monopole excitation and monopole ionization by Carlson et al⁽¹⁰⁸⁾ or electron shake-up and shake-off by Siegbahn et al⁽¹⁰⁹⁾. These processes can lead to many low intensity satellite lines and are most easily seen on the X-ray photo-electron spectra where they appear as a satellite peak shifted down from the main photo-electron peak.

I.2.4.3 The Auger Electron Energy

The Auger electron energy is simply the difference in energy before and after the Auger electron emission.

$$\text{i.e. } E_{ABC} = E_{\text{initial}} - E_{\text{final}}$$

The initial energy is the binding energy at the core electron (E_A). The value for E_{final} obtained by adding the one electron binding energies for the B and C levels is found to be too low to fit experiment. The effect of removing one electron reduces the screening and so increases the

binding on the other electrons. A good approximation enabling the experimental value to be predicted was suggested by Burhop⁽⁸⁸⁾. The binding energy of a singly charged ion is similar to that of the equivalent electron in the atom of next higher atomic number.

Chung and Jenkins⁽¹¹⁰⁾ discuss modifications to the method; for cases where the final double ionised state can be reached along two paths the mean value of the binding energies of the two equivalent electrons is taken and gives good agreement with the experimental values.

The binding energies of the atomic levels have been tabulated by Bearden and Burr⁽¹¹¹⁾ from photo-electron energy data.

All possible Auger transitions have been tabulated by Coghlan and Clausing⁽¹¹²⁾ using the Chung and Jenkins method.

I.2.4.4 Auger Line Intensity

The production of core holes in the subshells of a shell is almost proportional to the occupation numbers, e.g. for the L shell the occupation numbers and thus ionization probability is in the ratio 1 : 1 : 2 for L_1 : L_2 : L_3 . These core holes may undergo X-ray or Auger de-excitation involving electrons from higher shells, or the L_1 and L_2 holes may transfer to a higher subshell in the Coster-Kronig mechanism which is very rapid (and thus probable) when energetically favourable. This process, deduced by Coster and Kronig⁽¹¹³⁾ in 1935, accounts for the unexpected weakness of Auger transitions from these lower subshell core holes. The vacancy distribution of L holes becomes 1 : 15 : 25 for

$L_1 : L_2 : L_3$. The M shell is similarly affected by this process between the 5 subshells.

Calculations of transition rates have been made and tested against published spectra. The set of spectra by Physical Electronics Industries⁽¹¹⁴⁾ may be used to show the relative heights of Auger peaks of similar elements. McGuire^(115,116) has shown that the transition rate also depends on the number of electron configurations in the final state.

The occurrence of Coster-Kronig transitions from L_1 to $L_{2,3}$ in phosphorus (as GaP) has been shown by Tracy⁽¹¹⁷⁾. The yield curve of the P $L_{2,3} M_{2,3} M_{2,3}$ transition was plotted against the primary beam energy and rose steadily from zero at 132 eV, the threshold (binding energy) for the $L_{2,3}$ level. At 189 eV the yield curve turned upwards indicating that the L_1 level, which could now be ionized, was contributing to the $L_{2,3}$ ionization by Coster-Kronig transitions.

I.2.4.5 Excitation causing Auger Transitions

The energy used to form the initial core hole in the surface atom may come from several sources. The cloud chamber tracks observed by Auger resulted from X-ray excitation of inert gases and this method of creating core holes is used in the X-ray photo-electron spectrometer. Core holes are also produced by neutrons, protons, electrons and any radiation of sufficient energy.

I.2.4.5.1 X-ray Excitation

X-ray induced Auger spectra are advantageous where a surface is subject to degradation by an electron beam. The spectra

may be recorded directly as an energy distribution, $N(E)$ versus E , as the large background of variously scattered electrons is not present. However, the Auger signal level is low due to the smaller cross section of X-rays and the low intensity and difficulties in focusing X-ray beams. The cross section for X-rays varies considerably from element to element as the adsorption edges are traversed when the X-ray energy closely matches the core electron binding energy.

An Auger spectrum of GaAs using Al $K\alpha$ X-rays was recorded by Smith and Huchital⁽¹¹⁸⁾ and when compared with the integrated $dN(E)/dE$ versus E spectrum obtained by Tracy⁽¹¹⁷⁾ the peaks were found in the same positions, but the ratio of peak heights GaL_3 / AsL_3 was less in the X-ray than the electron beam case. This was interpreted as being due to the high cross section of the AsL_3 level (Binding Energy B.E. = 1323 eV) relative to the GaL_3 level (B.E. = 1115 eV) for the Al $K\alpha$ excitation at $h\nu = 1486$ eV. The surfaces were thought to have the same stoichiometry, as Tracy's sample produced the same electron stimulated $dN(E)/dE$ versus E curve as Uebbing and Taylor⁽¹¹⁹⁾ had recorded for a sample prepared in a similar way to that of Smith and Huchital.

The variable nature of the Auger emission with X-ray energy has been used to advantage by Henke⁽¹²⁰⁾ who used ultrasoft X-rays of ^{suitable} energy to obtain well separated photo-electron lines and Auger lines. The energies can be arranged to give good experimental conditions for high resolution and has enabled loss peaks to be observed for valence electron density calculations.

Many high resolution X-ray excited Auger spectra have been reported recently. The high resolution is complemented by appearance of the photo-electron lines which have accurately known positions and which can be used to calibrate the energy scale for lesser known Auger peaks. The errors introduced by determining the peak in the energy distribution curve from the differential curve obtained from electron beam instruments are also avoided. These reports describe high resolution, high vacuum ($\sim 10^{-6}$ torr) instruments which cannot maintain a high degree of surface cleanliness.

Yin, Yellin and Adler⁽¹²¹⁾ have accurately determined the LMM Auger lines for Cu, Ni and Fe, and by using the photo-electron spectra as a measure of the vacancy distribution created by the X-rays have assigned the three prominent Auger lines as type L_3MM . Schön⁽¹²²⁾ has carried out a higher resolution study of copper and showed that the fine structure revealed was not solely due to plasmon loss events as similar splitting has been observed in gaseous krypton (Siegbahn⁽¹²³⁾) and so may be a characteristic of the 3d band.

X-ray excited core holes may be formed as a secondary process following fluorescence de-excitation of an electron beam created core hole. As described earlier the probability of this is extremely low at low energies.

I.2.4.5.2 Proton Induced Ionization

This method of excitation has been reported by Musket and Bauer⁽¹²⁴⁾ and is of some importance in quantitative measurements as it does not suffer from the electron excited back-scattered electrons which enhance the yield of a primary

electron beam. However the need for an accelerator, and the low currents available, make this method less convenient than electron beam excitation.

I.2.4.5.3 Electron Induced Ionization

Electron beams are used most commonly to excite Auger electrons; these beams are easily produced with energies of several keV and currents of $\sim 100\mu\text{A}$ and may be focussed and deflected electrostatically. The electrons interact strongly with a solid and scattering occurs within a few interatomic distances of the surface. The dissipation of most of the beam power ($\sim 0.3\text{ W}$) in the small volume bounded by the beam cross sectional area ($\sim 1\text{mm}^2$) and the penetration depth can cause sufficient local heating to modify the properties of interest in the surface. Where this effect is unimportant the high efficiency of the electron beam in producing core holes results in a high Auger electron current which is relatively easily recorded. The presence of the high energy rediffused backscattered electron current must be considered in the detection system. These scattered electrons can be responsible for additional production of core holes and so modify the anticipated cross sections for ionization.

I.2.4.6 Ionization Cross Sections for Electrons

The ionization cross sections for atoms of solid surfaces are not simply obtained from the Auger electron currents measured after irradiation by a known electron beam current. Allowance must be made for backscattered electrons, elemental concentration and scatter of Auger electrons before they

reach the surface to escape.

These problems are avoided in gas studies as carried out by Glupe and Mehlhom⁽¹²⁵⁾.

In this work the Auger electron current was plotted against the energy of the electrons from a constant current electron gun and showed that the greatest yield, and thus greatest cross section, occurred at a beam energy of ~ 4 times the ionization energy of the level. The rise to this maximum was rapid from lower energy but the decrease was gradual at higher energy. The agreement between the gases studied was high despite the range of a factor of 10 in the absolute Auger yield.

The ionization cross sections for solids have been estimated by Bishop and Rivière⁽¹⁰⁶⁾ from an expression derived from the Born approximation by Worthington and Tomlin for X-rays. This curve approximately matches the experimental data showing a maximum cross section when the reduced energy (ratio of beam energy to core electron energy level) is between 2 and 3.

I.2.4.7 Backscatter Effects

The predicted ionization cross section will not be reflected directly in the Auger yield as the atoms releasing the observed Auger electrons, i.e. those within a few interatomic distances of the surface, are bombarded by both incoming electrons from the beam and backscattered electrons from the bulk. For a film of N atoms cm^{-2} of up to 1 monolayer Bishop and Rivière suggest that the probability (n) of an emission of a film Auger electron per incident beam electron

is:-

$$n = Nr \csc \theta (1-w) \bar{\Phi}(E_p, E_a) \quad \text{--- (I.1)}$$

where r is the factor raising the beam current to correct for backscatter.

θ is the angle from grazing incidence of electron beam.

$\bar{\Phi}(E_p, E_a)$ is the cross section of electrons in level E_a for electrons of energy E_p .

w is the probability of fluorescence de-excitation.

This backscatter current must originate in, and so be a property of, the substrate.

Calculations by Bishop of r for higher energy electrons shows that the value rises both with atomic number and primary beam energy and is not largely affected by angle of incidence.

The dependence of r on beam energy in the range 0.2 - 1.0 keV has been demonstrated by Houston and Park⁽¹²⁶⁾. They measured the Auger Ni(65 eV) signal, normalised for beam current, and found it increased rapidly with beam energy; the total secondary current above the ionization threshold was seen to increase in a very similar manner. This result, although not corrected for changes in ionization cross section with energy showed the rapid increase in Auger current due to backscatter at reduced energies of 3 - 10.

The enhancement of Auger yield due to backscattered electrons has been discussed by Gallon⁽¹²⁷⁾. His Auger yield from bulk silicon was due to electrons from incident beam and those backscattered and he suggested that this may

be written:-

$$I_a(E_p) = C I_p (\bar{\Phi}(E_p, E_a) + \alpha \beta) \quad \text{--- (I.2)}$$

where $I_a(E_p)$ is the Auger current for beam energy E_p

C is a constant

I_p is the incident electron beam current

$\bar{\Phi}(E_p, E_a)$ is the cross section of electrons in level E_a for beam energy electrons

β is a geometrical term

α is the cross section integrated over the range of energies present as backscatter current

defined as:-

$$\alpha(E_p) = \int_{E_a}^{E_p} \bar{\Phi}(E) N(E) dE \quad \text{--- (I.3)}$$

E_a is the energy at the Auger threshold (core ionization level)

$\bar{\Phi}(E_p, E_a)$ is initially equated to $\frac{I_a(E_p)}{C I_p}$ with an

estimated value for C , the collection efficiency for Auger electrons.

This value is then used in equation I.3 to obtain a value for $\alpha(E_p)$ and an iteration process started by substituting for α in I.2. This is continued until sufficient convergence is found. Gallon obtained 0.1% convergence in 4 iterations which indicates a low backscatter contribution.

This correction for backscatter reduces the rate of decay of ionization with rising beam energy but is of such a small effect that for beam reduced energies (E_p / E_a) of ~5 or 10 the Auger yield is very nearly the relative electron ionization cross section.

A further study of bulk silicon by Neave, Foxon and Joyce⁽¹²⁸⁾ gave similar Auger yields. They calculated the cross section $\bar{\sigma}(E_p, E_a)$ using the method described by Bishop and Rivière and used the value in equation I.2 and obtained values different from experiment. However if a factor K was introduced modifying the backscattering term equation I.2 becomes:-

$$I_a = CI_p(\phi + K\alpha\beta) \quad \text{--- (I.4)}$$

This only predicts the experimental values for high values of K implying that although the backscatter current is small ($\sim 10\% I_p$) it causes most of the Auger current. This discrepancy with the results of Gallon may be due to the error in the calculated value for the variation of cross section with reduced energy which should peak at a higher energy and tails off more slowly at high energy to match Gallon's results.

Backscatter contributions to the signal from carbon, nitrogen, oxygen, and sodium adsorbed on tungsten have been calculated by Gerlach and DuCharme⁽¹²⁹⁾ from their measured ionization cross sections and showed that less than 25% of the apparent carbon cross section was due to backscatter at reduced energies below 4.

These absolute cross sections, when plotted show that the cross section for a K level is proportional to the size the shell presents to the incident electron.

I.2.4.8 Auger Yield with Angle of Incidence

Although the first Auger spectra obtained from LEED systems utilised the normal incidence gun, Palmberg⁽¹³⁰⁾ studied

the effect of beam angle of incidence. He found the signal was increased towards glancing incidence and the signal from surface carbon became larger than the substrate palladium until surface roughness became significant at $\sim 7^\circ$. The simple model explaining this process is shown in Figure I.4. The escaping Auger current from a small volume of the solid is a function of the incoming current, which depends on the distance along the beam direction from the surface to the volume, and the probability that the Auger electrons reach the surface without suffering inelastic collisions, which depends on the shortest distance from the volume to the surface. The higher energy exciting beam has a considerably greater mean free path than the Auger electrons which limit the sampling depth.

If the intensity of the exciting beam is considered to be unchanged on passing through the surface region the slab model predicts an Auger signal versus angle of incidence:-

$$I_a(\Theta) = I_a(90^\circ) \csc(\Theta) \quad \text{--- (I.5)}$$

where Θ is the angle of incidence (surface to beam). When applied to an overlayer film this function will predict an equal increase in both film and substrate signal. If allowance is made for the absorption of the exciting beam, equation I.5 should approximately describe the signal from a thin film but the substrate signal will not rise as quickly with decrease angle of incidence and will eventually fall as all the beam is scattered by the film. The correct function is further modified by the effects of any changes

in backscattering.

This model becomes inaccurate if the primary beam becomes scattered from its incidence angle within a very short distance of the surface.

Harris⁽⁹⁶⁾ carried out systematic measurements of the Auger yield at different angles of incidence and emission from a dirty molybdenum surface. The current collected at 30° from the sample surface showed an approximately $\sin(\Theta)$ function where Θ is the beam angle of incidence to the surface. For a fixed angle of incidence of 30° to the surface, the molybdenum signals varied as $\sin(\chi)$ where χ is the collection angle from the surface but the carbon signal on the dirty surface decreased more slowly with reduction of angle χ and the sulphur signal on a heat treated surface increased with angle χ from $\chi = 90^\circ$ to 20° after which it dropped rapidly as χ approached 0° .

In the analysis of these results and discussion with Bishop and Rivière^(97,98) it was shown that for specific emission angle detectors (CMA or sector) surface materials give greatest signals at low collection angles to the surface with a normal incidence electron beam. However a wide angle detector (LEED optics used as a retarding field analyser) is best operated at a low beam angle of incidence where the reduced direct ionization is more than compensated by an increased backscatter factor.

I.2.4.9 Chemical Shifts Observed by A.E.S.

A large proportion of the equipment in present use has insufficient resolution and accuracy to determine the position

of peaks and the slight shifts associated with different bonding states. However this situation is changing, encouraged by the results of ESCA machines.

Haas and Grant^(131,132) set up a 4 grid (LEED optics) retarding field analyser and, by careful elimination of magnetic fields and centering the sample, detected different Auger spectra for the KLL transitions for carbon on Mo(110) depending on whether it was a carbide formed as the molybdenum was heated in vacuum and carbon diffused to the surface or as carbon monoxide adsorbed on a clean surface.

Shifts of up to 6 eV were observed by Grant and Haas⁽¹³³⁾ when they oxidised a Ta(110) surface. The shift was observable within one monolayer of oxide as determined by LEED. The shift towards a higher binding energy was in agreement with Siegbahn's results⁽¹²³⁾ for oxidation of metals and increased with oxygen coverage. They note that work function changes in the target do not affect the measured peak positions as the target and grid are electrically connected (and thus have equal Fermi levels).

Bishop, Rivière and Coad⁽¹³⁴⁾ detected a sharp change in the relative peak heights due to titanium atomic level transitions between the clean and oxidised states. This change was found to occur in the opposite direction when sulphur was adsorbed. The 3 peaks involved were assigned to 0, 1 and 2 valence electrons. The 24 eV $M_{2,3}$ VV peak disappeared on oxidation either due to direct screening by surface oxygen or loss of valence electrons. Plasma loss peaks from the major titanium peaks were found to be dependent

in size and position on the state of oxidation.

Different states of oxidation of vanadium were studied with A.E.S. by Szalkowski and Somorjai⁽¹⁸⁾. They found a shift of $+0.6 \text{ eV}$ in core binding energy per vanadium oxidation number in the $L_{2,3}$ inner core transition. The shift in energy for transitions involving the valence band was smaller and less consistent.

I.2.4.10 Quantitative Use of A.E.S.

A.E.S. is used extensively for qualitative detection of surface components but it is more useful if accurate values of amounts and distributions of these materials can be related to Auger spectra. Quantitative results may be divided into three aspects:- lowest detection limits, surface films of less than one monolayer (M-L), and thicker films where the Auger electrons from internal atoms have to escape to the surface.

There have been several estimates of the surface density of species at the limit of detection of A.E.S. The theoretical limit for a LEED-Augur 4 grid analyser is given by Chang⁽¹³⁵⁾ as $10^{12} \text{ atoms cm}^{-2}$ and this limit has been obtained for carbon and silicon, and oxygen on silicon (Chang⁽¹³⁶⁾). Quinto, Sundaram and Robertson⁽¹³⁷⁾ have used a similar method to Chang to obtain the limit for carbon on nickel in their 3 grid LEED-Augur system as $1.7 \times 10^{14} \text{ atoms cm}^{-2}$. This represents a film of 0.1 M-L at the Ni substrate surface. Using the results of Bishop and Rivière⁽¹⁰⁶⁾, that ionization cross sections are inversely proportional to the square of the critical ionization po-

tential, the limit for sulphur is 0.03 M-L.

For surface films of up to 1 M-L the theory of Bishop and Rivière may be used; this predicts a linear increase of the Auger current from the film with increasing coverage of the substrate. Ibach, Horn, Dorn and Lüth⁽¹³⁸⁾ followed the adsorption of oxygen on Si(111) and were able to determine many factors affecting the sticking probabilities of between 2×10^{-4} and 10^{-1} . Ertl and Küppers⁽¹³⁹⁾ used A.E.S. to follow the build-up of carbon monoxide on copper/nickel alloys. In cases of thin overlayers simple standardising of the spectra gives coverages directly.

1.2.4.11 Quantitative Comparisons of Auger Current

Absolute Auger yields of surface atoms are obtained from many measured and calculated parameters. However, the relative yields of surface species and various thicknesses of overlayers may be directly measured if the Auger analyser and exciting electron beam conditions are kept constant for the series of comparisons. The spectra are plotted as the derivative of the energy distribution curve and, using the method described by Weber and Johnson⁽¹⁴⁰⁾, the Auger current is directly proportional to the sum of the positive and negative going excursions of the line away from the background shape. The changes of substrate and overlayer Auger currents with film thickness are required to calculate the Auger electron mean free paths, which are essential to the interpretation of A.E.S. data. The sensitivity of the method depends on the depth in the solid from which Auger electrons escape with no significant change in energy.

As is discussed in section I.2.6 the Auger electron mean free path calculation depends heavily on the accuracy of the method employed to calibrate the surface film quantity.

The first report of sensitivity of the method was by Weber and Peria⁽⁹⁹⁾ who detected 1/10 M-L of caesium evaporated on silicon. Palmberg and Rhodin⁽¹⁴¹⁾ then assessed the escape depths through silver overlayer films grown on gold on a magnesium oxide substrate. The calibration point was taken as the deposition to cause conversion of the Au(100)-(5x1) LEED pattern to the Au(100)-(1x1)-Ag as equal to one monolayer. They assumed that film growth was in complete monolayers and the Auger signals from the surface and substrate metals would rise and fall exponentially. Their results gave a mean escape depth through silver of 2 M-L for 72 eV electrons and 4 M-L for 362 eV electrons. Gold deposited on silver at room temperature showed the rate of fall of the silver peak equal to the rate of rise of the gold peak. This indicated island growth of the overlayer with islands sufficiently thick to shield any Auger electrons from the substrate. If the silver peak at no coverage was normalised to the gold peak at complete coverage the sum of the two peaks due to intermediate coverages of gold was a constant. This showed thick island growth if the two escape depths of 72 and 362 eV electrons were not identical; they had been shown to differ by a factor of 2 in silver.

The escape depths determined by Baer, Heden, Hedman, Klasson and Nordling⁽¹⁴²⁾ for X-ray excited electrons of about 1.2 KeV energy from chromium and gold during the

overgrowth of a gold film on a polished, oxidised chromium surface were $22 \pm 4 \text{ \AA}$. The similar energy electrons from the two metals gave a constant normalised sum of the two peak heights, which, by the argument of Palmberg and Rhodin, gave no measure of surface layer growth characteristics. The film deposition was calibrated as a chopped fraction of a second film of sufficient thickness ($>200 \text{ \AA}$) for interferometric measurement.

A useful model for use in the analysis of A.E.S. results from many-layered surface films was proposed by Gallon⁽¹⁴⁴⁾. The primary beam containing " N_0 " electrons/sec has a probability " P " that each electron will be scattered by a given atomic layer. Any scattered electron has a probability " A " that it will create a given Auger electron which then has a probability " E " of escape through each layer to the surface.

An unattenuated beam passing through such a layer structure will give Auger electrons:-

$$\begin{aligned}
 \text{From 1st Layer} &= N_0 P A && \text{electrons/sec} \\
 \text{2nd Layer} &= N_0 P A E(1-P) \\
 \text{3rd Layer} &= N_0 P A E^2(1-P)^2 \\
 \text{nth Layer} &= N_0 P A E^{n-1}(1-P)^{n-1}
 \end{aligned}$$

The total Auger current due to one type of Auger transition in ' n ' layers

$$= N_0 P A \left[\frac{1 - (1-P)^n E^n}{1 - (1-P) E} \right]$$

For very many layers

$$\text{Then } I_{\infty} = N_o P A \left[\frac{1}{1-(1-P)E} \right]$$

For n layers

$$I_n = I_{\infty} \left[1 - \left(\frac{1-I_1}{I_{\infty}} \right)^n \right]$$

This model oversimplified the processes occurring in the surface but the omission of backscatter current did not affect the result of the last equation if the incident electron beam was taken as constant current with depth and this current made the sum of the incident and backscatter currents. The model closely fitted the results of Palmberg and Rhodin and showed that ~80% of the silver 362 eV peak originated in the first 6 layers.

The results of Charig and Skinner⁽¹⁴⁴⁾ for nickel evaporation on silicon from a heated nickel filament showed an initial linear rate of increase of the nickel 54 eV and decrease of the silicon substrate 89 eV peaks with exposure time (assumed to be proportional to coverage) until a coverage which may be calculated from the data shown to be ~2.7 Å average film thickness. They attribute this to monolayer island growth. The Auger signal rate of change then decreased to (deposition time)^{2/3} which they attribute to the growth of spherical cap nuclei. Their analysis of their results implies a sticking probability of 0.4 for nickel on silicon at room temperature relative to that of nickel on glass which had been used as a calibration. The Auger signal from the substrate silicon was then stopped by a single

monolayer of nickel - a silicon 89 eV mean free path in nickel of less than 3 Å.

However, these results appear to satisfy Gallon's model extended later by Jackson, Gallon and Chambers⁽¹⁴⁵⁾ in which, for materials which grow in complete monolayers, the change of slope marks the completion of a monolayer. This assumption then makes the sticking probability for nickel on glass similar to that on silicon. The discontinuity at the change of slope is greatest at the end of the first monolayer, but may not be observed if the sticking probability increases on completion of the layer. A change of sticking probability also changes the deposition time between discontinuities under constant deposition conditions. In support of their model these authors presented results for silver evaporated on nickel which was grown epitaxially on freshly cleaved rock salt. The Auger signal from the silver was found to rise linearly with deposition time until ~40% of the thick film value when rate of rise was reduced. The scatter on the results did not allow further linear portions of the graph to be determined. The results showing the decay of the nickel signal are not consistent in both graphs shown; only one is clearly linear. If this discontinuity in the graph corresponded to the first monolayer, the sticking probability for silver on nickel at room temperature was 0.7 ± 0.2 , and the escape depth for 355 eV electrons in silver was 5.4 ± 0.6 Å.

Evaporation of iron on silicon carried out by Ridgeway and Haneman⁽¹⁴⁶⁾ did not produce a linear increase in the iron, 44/46 eV Auger current. The significance of the initial

approximately linear decrease of the silicon 91 eV peak could not be assessed from the results shown. The errors associated with the method of calibration employed here are discussed in section I.2.6. These results corroborate the errors suggested above in Charig and Skinner's calibration.

In the quantitative A.E.S. study of sulphur adsorption on nickel crystals by Perdereau⁽¹⁴⁷⁾ the surface sulphur level was detected by labelling H_2S with ^{35}S . He recorded a closely linear response of nickel Auger 62 eV current against the metered current to earth from the crystal, i.e. Auger current (Ni 62 eV) $\propto I_p - I_s$.

where " I_p " is the primary beam current to the crystal.

" I_s " is the total current leaving the crystal face.

This response was identical for both the (100) and (111) face of nickel. On plotting the Auger response to sulphur normalised to the nickel 62 eV peak size the 5 points shown were represented as a straight line in the range 0-1 monolayers. This showed that if the Gallon monolayer growth model could be applied to this case the screening effect of sulphur to the nickel Auger electrons was low. High screening by the sulphur would attenuate the nickel signal at high coverage, raising the sulphur/nickel response from the linear absolute sulphur signal.

Seah^(148,149) reviewed quantitative A.E.S. before April 1972 and extended Gallon's theory, written as

$$I_n^s/I_0^s = \exp(-n/nc)$$

where I_n^s is the signal from the substrate with n atomic overlayers

I_0^s is the clean substrate signal

n is the number of overlayers

nc is the inelastic mean free path for substrate Auger electrons through the overlayer material.

Similarly

$$I_n^c/I_\infty^c = 1 - \exp(-n/nc)$$

where the subscript n refers to n layers

" " ∞ " " bulk material

" superscript c " " condensate signal.

Seah applies no correction for the change in nc due to the change in energy of the condensate Auger electrons.

When a low atomic number material is condensed onto a high number material the condensate Auger signal curve rises more slowly than the above relationship as the relatively high backscatter current from the substrate decreased in effect. Gallon had assumed this current would be constant for his model.

Seah also considered the effects of the condensation behaviour found in real films. The monolayer growth used as the basis for earlier models only occurs if bulk diffusion is negligible and surface diffusion operates. However, for most experiments the substrate temperature is too low and arriving atoms remain on the surface plane without completing earlier layers. The resulting "holes" in the overlayer film allow the substrate signal to persist longer than

expected. He calculated that the fractional coverage of the 'm'th layer after the deposition of the equivalent of n full monolayers resulting from such a method of growth is

$$\Theta_m = 1 - (\exp(-n)) \left(1 + n + \dots + n^{m-1} / (m-1)! \right)$$

The condensate Auger electron current from this growth is

$$I_n^c = I_o^c (1 - \exp(-n/n_c^{-1}))$$

where $n_c^{-1} = (1 - \exp(-1/n_c))^{-1}$

similarly

$$I_n^s = I_o^s \exp(-n/n_c^{-1})$$

Seah found by numerical substitution that the effective coverage of thick films forming incomplete monolayers was $\frac{1}{2}M-L$ less than the complete monolayer calculation. The detected inelastic mean free path is also dependent on the trajectory of the Auger electrons through the surface film. Each A.E.S. detecting system selects a wide or narrow acceptance angle for electrons from the target; most analysers accept a wide range of incident angle electrons and give results which may be used interchangeably. The normal and high collection angle C.M.A. and LEED optics retarding field analyser result in a mean free path of $\frac{3}{4}$ of the direct path escape depth.

I.2.4.12 Interpretation of Platinum Auger Spectra

Platinum was one of the materials studied by Haas, Grant and Dooley⁽¹⁵⁰⁾ who designated their experimentally determined peaks as:-

Observed Energy (eV)	Transition
152	$N_5^N N_6^N N_6$
160	$N_5^N N_6^N N_7$
172	$N_5^N N_7^N N_7$

As these transitions occur with the same principal quantum number for initial and first re-arrangement core holes they are Coster-Kronig events and occur with a high probability. Below 50 eV they recorded peaks at 12, 24 and 43 eV.

Gland and Somorjai⁽¹⁷⁾ labelled the following peaks:-

65 eV	$N_6, 7^O 4, 5^O 4, 5$
150/160/170 eV	$N_4, 5^N N_6, 7^N N_6, 7$
239/253 eV	$N_4, 5^N N_6, 7^O 4, 5$

The K, L and M Auger and L Coster-Kronig transitions in platinum which largely occur at energies over 1 keV, have been listed by Toburen and Albridge⁽¹⁵¹⁾ from their studies of excited states resulting from the decay of ^{195}Au .

A comprehensive list of possible Auger transitions for the elements, including platinum, has been published by Coghlan and Clausing⁽¹¹²⁾ using the mean levels of the Z and z+1 elements for B and C levels as described for copper.

1.2.4.13 Interpretation of Copper Auger Spectra

A review of the results and interpretation of LMM Auger transitions in copper was published by Schön⁽¹²²⁾. Most previous work^(121, 137, 141, 152, 153) had been carried out at a relatively low energy resolution but the work of Jenkins and Chung⁽¹⁵⁴⁾ showed splitting of the 62 eV MMM peak into

two components and detail in the LMM transitions. They attributed the peak intensity ratios of $L_3^{MM} > L_2^{MM} > L_1^{MM}$ to Coster-Kronig transitions. They obtained a good agreement between experimental and calculated peak positions using the relationship:-

$$E_{ABC}(Z) = E_A(Z) - \frac{1}{2}(E_{B(Z+1)} + E_{B(Z)}) - \frac{1}{2}(E_{C(Z+1)} + E_{C(Z)})$$

The transitions and energy values are listed in Table I.1 Further work by Jenkins and Chung⁽¹⁵⁵⁾ showed that the MMM doublet was not only accompanied by plasmon loss doublets about 7.5 eV and 15 eV below the main peaks but also a doublet above these indicating a plasmon gain. They could not determine if the event was due to surface or bulk plasmons.

The energy scale for spectra obtained using X-ray excitation was accurately fixed by Yin, Yellin and Adler⁽¹²¹⁾ who used the photo-electron peaks as a calibration of their spectrometer. Allowance must be made when comparing peak energy positions in the energy distribution mode and the derivative mode in which the high energy minimum is taken as the peak position.

Yin, Tsang, Adler and Yellin⁽¹⁵⁶⁾ determined a plasmon loss energy for cleaned copper as 13 eV. Where such losses could not explain their observed fine structure, particularly in the L_3^{MM} peaks, they confirmed that the lines were Auger transitions by comparison with krypton spectra and that the shifts were due to spin-orbit coupling to the valence vacancies.

I.2.5 Sample Cleaning

The surface sensitivity of A.E.S. to contamination and the

Transition	Calc. (eV)	Obs. (eV)	Transition	Calc. (eV)	Obs. (eV)
$L_1 M_5 M_5$	1085	1090	$L_3 M_3 M_5$	846	
$L_1 M_4 M_5$			$L_3 M_3 M_4$		
$L_1 M_4 M_4$			$L_3 M_2 M_5$	845	843
$L_1 M_3 M_5$	1011		$L_3 M_2 M_4$		
$L_1 M_3 M_4$			$L_1 M_1 M_1$	839	
$L_1 M_2 M_5$	1010		P		
$L_1 M_2 M_4$			$L_2 M_1 M_5$	817	815
$L_1 M_1 M_5$	962		$L_2 M_1 M_4$		
$L_1 M_1 M_4$			$L_3 M_1 M_5$	797	800
$L_2 M_5 M_5$	940	939	$L_3 M_1 M_4$		
$L_2 M_4 M_5$			$L_2 M_3 M_3$	792	
$L_2 M_4 M_4$			$L_2 M_2 M_3$	791	791
$L_1 M_3 M_3$	937		$L_2 M_2 M_2$	790	
$L_1 M_2 M_3$	936		$L_3 M_3 M_3$	772	
$L_1 M_2 M_2$	935		$L_3 M_2 M_3$	771	772
$L_3 M_5 M_5$	920	919	$L_3 M_2 M_2$	770	
$L_3 M_4 M_5$			$L_2 M_1 M_3$	743	
$L_3 M_4 M_4$			$L_2 M_1 M_2$	742	735
P			$L_3 M_1 M_3$	723	
$L_1 M_1 M_3$	888		P		
$L_1 M_1 M_2$	887	885	$L_3 M_1 M_2$	722	717
$L_2 M_3 M_5$	866		$L_2 M_1 M_1$	694	690
$L_2 M_3 M_4$			$L_3 M_1 M_1$	674	679
$L_2 M_2 M_5$	865	864			
$L_2 M_2 M_4$			$M_1 M_4 M_5$	109	109
			$M_2 M_4 M_5$	63	62
			$M_3 M_4 M_5$	61	59

TABLE I.1 Copper Auger Peaks (Jenkins and Chung).

sensitivity of LEED to atomic spacing at the surface have shown that a "clean ordered surface" is approachable but not attainable.

Except for materials such as mica, magnesium oxide and silicon (Grant and Haas⁽¹⁵⁷⁾), which may be cleaved in the vacuum system the cleaning process is multi-staged. Metal crystals for LEED studies must be cut to expose the required face - the angle of cut being determined after a back reflection Laue X-ray measurement. The method generally employed to give minimum damage to a crystal is spark cutting followed by spark planing. This may be followed by mechanical polishing with a series of carborundum papers until only fine marks remain. If the crystal is not supported in a mounting plastic the face may become bowed and the orientation lost when using abrasive papers. However, the use of mounting plastic allows large particles of abrasive to be carried in air holes in the plastic and these may cause scratches at a later stage. Final polishing may be carried out with diamond and/or alumina powders on polishing cloths. Diamond produces a better flat surface than alumina which appears to redistribute the surface material rather than cut it away.

After polishing, the surface damage must be removed, usually by etching or electropolishing until an undamaged surface is revealed but before deep etch pits are formed.

Further cleaning must be carried out in the vacuum system where the improved surface can be maintained. Heating a sample for many hours may anneal damage from the surface and allow high vapour pressure contaminants to escape.

However, for most metals annealed at $>800^{\circ}\text{C}$ the surface becomes enriched with carbon and sulphur which diffuse from the bulk. Prolonged argon ion bombardment may be used to sputter these impurities away, while combined bombardment and high temperature annealing may reduce the bulk impurity level through surface enrichment and surface cleaning.

Surface impurity removal by annealing in oxygen followed by reduction in hydrogen has been found to be adequate for a nickel(110) surface (Owens⁽²⁵⁾) but the apparently clean platinum(100) surface obtained by oxygen treatment has been found to differ from that obtained by argon ion bombardment of a hot crystal by Grant and Haas⁽⁶⁸⁾.

1.2.6 Quartz Crystal Monitoring of Evaporation

In a study of the Auger effect from very thin films it was necessary to devise a calibrated monitor to determine the mass of evaporated metal deposited on a substrate. The quartz crystal oscillator has been well tested in this role and is sufficiently sensitive and accurate for the very low masses deposited in such a study.

In this method a suitably cut quartz crystal with evaporated metal electrodes is supported so as to receive a constant proportion of the evaporated metal flux emitted by a source to a substrate. The natural oscillation frequency of the crystal is changed by the loading of the film and this change may be related, by calculation or calibration, to the film thickness on the substrate.

The characteristics of quartz crystals vary with the angle of cut relative to the crystallographic axes and are

described by Vigoureux and Booth (158) and Heising (159).

The quartz crystal may be cut in many ways to give required features. A plate cut perpendicularly to the optic(Z) axis (i.e. Z-cut) has no piezo-electric properties but any other cut will exhibit some piezo-electric effects. The simplest cut, X-cut, is perpendicular to the electrical axis and so will readily undergo longitudinal vibrations but as this will frequently excite the harmonics of lower frequency modes its frequency is unreliable. The Y-cut will vibrate in a more stable shear thickness (transverse) mode but has a bad temperature coefficient of $86 \text{ ppm } ^\circ\text{C}^{-1}$. If cuts at angles between the Y-cut and Z-cut are made there are two angles which give zero temperature coefficients. These cuts, AT and BT, are close to the AC and BC cuts which have zero coupling with the interfering low frequency shear modes. Care must be taken that the plate dimensions of the AT and BT cuts do not encourage flexure modes. Both these cuts are suitable for thin film mass determination but the BT cut is thicker for a given frequency and so is easier to handle.

The crystals may be held in compression clamps which may suppress unwanted modes but reduce activity or by clips soldered at the edges of evaporated metal electrodes. In the latter case the contact point is maintained stationary by evaporating common terminal films to both sides of the plate.

In the analysis of the sensitivity of quartz crystals to evaporated films by Behrndt(160) it is implied that the

film is evaporated uniformly across the whole crystal. For thickness shear oscillations the plate is a half wave-length thick at the fundamental frequency. i.e:-

$$f = V_{tr} / 2t = N/t \quad \text{--- (I.6)}$$

where V_{tr} - transverse wave velocity (m sec⁻¹)

t - crystal plate thickness (m)

N - frequency constant (Hz m)

$$\text{but } t = m / \rho_q A \quad \text{--- (I.7)}$$

where ρ_q is density of quartz

A is area of quartz crystal face

m is mass of quartz crystal

therefore from I.7

$$dt = \frac{1}{\rho_q A} dm \quad \text{--- (I.8)}$$

from I.6

$$df = - \frac{N}{t^2} dt \quad \text{--- (I.9)}$$

I.8 substituted in I.9 and replacing t

$$df = - \frac{f^2}{N \rho_q A} dm = \frac{f}{m} dm \quad \text{--- (I.10)}$$

The frequency downward shift is proportional to mass change which, for thickness shear oscillations, is independent of material as the antinodal surface is not critical of the elastic properties of the overlayer. For small changes in mass the frequency shift due to the film will be the same as that caused by the same mass of quartz.

This analysis is not completely correct for most crystals where electrodes are evaporated onto each major face of the

plate but which overlap, and so excite, only ~50% of the crystal. A film evaporated on part of such a crystal must lie on the strongly oscillating part which may then be taken as area A in this analysis.

A similar analysis by Stockbridge and Warner⁽¹⁶¹⁾ reported by Greaves⁽¹⁶²⁾ gives the loaded frequency f_l as

$$f_l = f_0 \left(1 + 2K \frac{t_f}{t_q} \right)^{\frac{1}{2}}$$

where K is a constant near unity which depends on the mass distribution on the plate

t_f is the film thickness

t_q is the quartz thickness

This gives equation I.10 with an additional factor K and , the density of quartz, replaced by ρ_f , the density of the film.

Calibrations of Auger response to evaporated metal films monitored during deposition with quartz crystals have been reported. Ridgeway and Haneman^(146,163) evaporated iron and nickel onto a silicon substrate from filaments of the pure metals. The quartz crystal became the target when the silicon sample was withdrawn and was used to calibrate the flux from the source before and after deposition on the silicon. The stability of the AT-cut crystal was 1 in 10^8 before evaporation and its sensitivity was calculated using the method described above by Behrndt. As the film was, apparently, evaporated uniformly over the whole crystal this analysis is valid. The dimensions of the source and separation distances do not enable the errors in using an inverse

square law relationship to be estimated.

Seah⁽¹⁴⁹⁾ calibrated the response of a quartz crystal monitor by evaporating aluminium over the crystal and an adjacent optical flat to produce a step which was measured by a Talystep. Only one measurement is quoted; the corrections for different distances and angles to the source and different sticking probabilities on the quartz, molybdenum and glass are not discussed. A calculated frequency shift based on Behrndt's method was 18% higher. This discrepancy could indicate that although the film was evaporated over the area of the electrodes on the crystal the oscillating part of the crystal extends slightly beyond the electrodes and this area must also be covered to give the predicted shift

1.3 Further Background

1.3.1 The Pt(100)-(5x1) Surface Structure

Most materials studied with LEED exhibit a clean surface structure with the characteristics of the corresponding plane in the bulk unit cell. However, three metals, platinum, iridium and gold, exhibit a similar complex pattern on the (100) face when subjected to the commonly used cleaning techniques.

The first reported LEED study of the Pt(100) face, by Tucker⁽⁵⁰⁾ does not describe the clean surface pattern but subsequent reports by many other workers have shown a diffraction pattern which is labelled approximately as Pt(100)-(5x1)

by Hagstrom, Lyon and Somorjai^(14,15). Two papers by Fedak and Gjostein^(164,165) describe a similar structure on gold crystals:- Au(100)-(5x1). They considered the possible causes to be facetting, which did not particularly favour the very stable (5x1) configuration, or impurity atoms regularly spaced on, or included in, the surface, requiring unusually long range interactions. They proposed a surface active, bulk impurity derived overlayer of impurities. In a later paper, describing the use of a better resolution LEED instrument, Fedak and Gjostein⁽¹⁶⁶⁾ observed a splitting of the fractional order reflections into triplets and doublets with particularly bright spots visible in the positions corresponding to an exactly orientated Au(111) type hexagonal overlayer. They considered the diffraction effects from a square (100) substrate with a (111) overlayer and showed double diffraction would be characterised by a cut off of the Au(100) (10) reflections at an electron energy of 18.2 eV, the condition that the electron wavelength equals the surface mesh dimension. However, the (10) reflection could be observed down to 10 eV. They then proposed an Au(111) spacing overlayer coinciding with the (100) substrate after each (5x20) (100) meshes and carried out a structure factor analysis to attempt to explain the spot intensities. Only when the coordinates of the components of the superlattice were modulated across the coincidence mesh was a fair fit with experiment obtained; the errors were attributed to the square wave modulation used in the model.

Impurities were still thought to be present to overcome

the obviously energetically unfavourable growth of Au(111) directly on Au(100).

Palmberg and Rhodin⁽¹⁶⁷⁾ grew gold films on clean silver films in good U.H.V. conditions. By growing the films on KCl or MgO substrates diffusion of impurities was minimised while purity of the evaporant was checked by monitoring in a quadrupole mass spectrometer. They found an Au(100)-(5x1) formed after 3 monolayers (M-L) deposition of gold on a silver film exhibiting a Ag(100)-(1x1) pattern. The (5x1) pattern returned to a (1x1) after further deposition of 1 M-L of silver. Gold evaporated onto an Au(100) surface exhibiting a (5x1) pattern only resulted in a (5x1) pattern at temperatures above 0°C.

In a later paper⁽¹⁶⁸⁾ describing evaporation of monolayer quantities of gold and silver on Cu(100) and Pd(100) substrates Palmberg and Rhodin pointed out that as gold evaporated onto silver tended to aggregate; the figure of 3 M-L of gold before the Au(100)-(5x1) pattern appeared was an average figure for the whole surface. Although many measures were taken to reduce impurities in the films alkali ion emission was not monitored but was unlikely due to the electric fields present. Both silver and gold films evaporated onto a Cu(100) film took a hexagonal atomic arrangement. The modification to the silver atom spacing in the overlayer was small while the gold atomic spacing decreased by 5% in the Cu<100> direction. Gold grew pseudomorphically for 1 M-L on Pd(100) which was held at -50°C to reduce alloying. This required a reduction in gold atomic spacing

from its bulk value by 4.7%. Further evaporation of gold on Pd(100) produced Pd(100)-(1x7)-Au. Evaporation of 1 M-L of Ag, Pd or Cu on the Au(100)-(5x1) created the Au(100)-(1x1) structure.

The similar Pt(100)-(5x1) structure was ascribed by Lyon⁽³²⁾ to an overlayer with regularly spaced vacancies, the spot splitting resulting from the presence of antiphase domains. He observed simple splitting of the additional features into double spots and monitored their relative intensities under various conditions of formation. He explained Tucker's failure to report the Pt(100)-(5x1) by showing that cooling the crystal in oxygen caused the loss of the pattern. However, he did not quote the carbon monoxide partial pressure associated with the admission of oxygen to the system. The response of the surface to the presence of oxygen implied that the surface was contaminated, probably by carbon; Weinberg, Lambert, Comrie and Linnett⁽¹⁶⁹⁾ have shown that the rate of absorption of oxygen on a well cleaned Pt(111) crystal is very low but increases in the presence of impurities, particularly carbon.

Morgan and Somorjai⁽¹¹⁾ described a model in which the Pt(100)-(1x1) surface mesh was covered by a hexagon Pt(111) layer with one direction of close packed atoms of each layer aligned. This set the constraint of a 5% contraction in the overlayer in the direction perpendicular to the alignment. This model does not account for the simple splitting that they observed.

One of the earliest studies using A.E.S. was directed

towards solution of the cause of the anomalous surface structures on platinum and gold (100) crystal faces. Palmberg⁽³⁵⁾ detected no impurities on a Pt(100) crystal after removing a heavy coating of carbon by annealing in oxygen, and described the Pt(100)-(5x1) pattern as the clean surface pattern. He produced more clearly resolved LEED patterns which showed, from the appearance of a single domain pattern, that the composite was made up of 4 domains related as 2 pairs with 2 fold rotation symmetry and mirror symmetry between pairs. The resolution was adequate to enable Palmberg to index the spots as resulting from a Pt(100) ($\sqrt{29} \times \sqrt{70}$) surface mesh. He did not give a method by which a hexagonal overlayer reconstruction could be fitted to this coincidence mesh.

The only report that disagrees with the conclusion that the Pt(100)-(5x1) pattern is typical of a surface which is clean within the detection limits of A.E.S. is from Grant and Haas⁽¹³³⁾. They found that the Pt(100)-(5x1) pattern resulted from normal cleaning treatments in which annealing in oxygen was used to remove surface carbon. They confirmed that the modulated ring appearing after high temperature annealing was due to carbon in graphitic layers. Although this was removed after argon ion bombardment it reappeared on annealing to 900°C. However, to the detection limits of A.E.S., the carbon could be permanently removed from the sample if argon ion bombarded for 6 hr. while the crystal was maintained at 1200°C. This treatment was considerably more severe than that usually employed in surface cleaning.

The Pt(100)-(5x1) pattern observed after this treatment was modified to a Pt(100)-(1x1) over most of the crystal surface by annealing at 1100°C. This change was reversed by annealing at 700°C. The only difference in A.E.S. spectra observed between the surfaces exhibiting the two patterns was the diminution of the 27 eV peak when the Pt(100)-(5x1) pattern appeared. The Pt(100)-(1x1) pattern was not modified by the presence of oxygen up to 2×10^{-6} torr when at room temperature but changed to a strong Pt(100)-(5x1) in oxygen at 1200°C. The Pt(100)-(1x1) could not be regained after argon ion bombardment or annealing, but was obtained again after removing and etching the crystal in strong acids.

They conclude that the Pt(100)-(5x1) structure is associated with an impurity near the surface; this impurity is oxygen or is brought near the surface by diffusion in the presence of oxygen.

Joyner, Gland and Somorjai⁽¹⁷⁰⁾ have reviewed the cleaning procedures for platinum crystals. They describe the Pt(100)-(5x1) surface structures as a clean surface and the Pt(100)-(1x1) as impurity stabilised, usually by carbon. Their explanation, using a hexagonal overlayer, can only result in a true Pt(100)-(5x1) and not the split pattern observed. They do not recommend the use of argon ion bombardment in the cleaning procedure as it is inefficient in removing surface carbon, but use exclusively chemical cleaning in oxygen. They state that the appearance of the Pt(100)-(5x1) is a reliable indication of an atomically clean Pt(100) surface.

The parallel study of the Ir(100) was continued by Grant⁽¹⁷¹⁾. An Ir(100)-(1x1) resulted from cleaning solely by annealing at 1400°C but a true Ir(100)-(5x1) resulted from argon ion bombardment followed by annealing at 400°C. Unlike the Pt(100)-(5x1) surface structure the Ir(100)-(5x1) did not completely disappear on absorption of CO, CO₂ or O₂. When the Ir(100)-(5x1) pattern was visible an A.E.S. peak at 5 eV was found to be greater than when a Ir(100)-(1x1) was seen. This appearance of the Ir(100)-(5x1) was correlated with oxygen treatment.

Ignatiev, Jones and Rhodin⁽¹⁷²⁾ grew xenon crystals at 55°K on both the Ir(100)-(1x1) and (5x1) surface structures. On (1x1) the resulting Xe(111) growth showed 12 fold symmetry consistent with two domains growing with 2 fold symmetry on a square substrate. However, on the (5x1) surface only 6 fold symmetry was observed as the xenon crystal grew on a hexagon structure.

I.3.2 Alloys

The use of alloys to provide active surfaces for catalytic reactions is of growing importance as new theories of catalysis are developed. Alloys may be prepared to give a large range of interatomic spacings and electronic properties with greater variation than those of the pure metals. Although alloys have been studied extensively for bulk effects and the interatomic spacings determined using X-ray diffraction the surface properties have not been commonly determined using LEED or A.E.S. Indirect indications of discrepancies between surface and bulk atomic compositions

were found by Cadenhead and Masse⁽¹⁷³⁾ who studied hydrogenation of benzene over Cu/Ni, Cu/Pd and Au/Pd alloys. Moss, Gibbens and Thomas⁽¹⁷⁴⁾ studied thin evaporated alloy films (Pd/Rh) to ensure that phase separation and surface segregation did not occur during simple catalytic reactions.

Order-disorder transformations in the bulk of alloys are reviewed by Cohen⁽¹⁷⁵⁾, and more recently by Irani⁽¹⁷⁶⁾. This phenomenon, exhibited in many alloy systems, occurs as the alloy temperature is reduced below a critical level when the random solid solution changes as atoms take up specific lattice sites to form a long period superlattice. The appearance of superlattice features at surfaces may be important in catalytically interesting alloy systems. Irani and Cahn⁽¹⁷⁷⁻⁹⁾ have studied the particularly interesting CuPt system in which the copper and platinum atoms order below 815°C so that the (111) planes are filled alternately with the two metals. They have resolved the ordering process occurring in this case as a nucleation and growth (type 1) reaction where drastic atomic rearrangements occur in small volumes. The type 2 transformation, in which small atomic changes occur simultaneously throughout the alloy, was not found to occur. The two types of transition are characterised by the X-ray diffraction changes if the ordering is accompanied by a change in symmetry. A type 1 change will cause diffraction from both the growing nuclei and the unchanged volume while type 2 will cause a gradual broadening of the disorder features and slow growth due to the new ordered lattice. These changes should be similarly detected

at the surface by LEED.

Order-disorder transitions have also been studied in the Field Ion Microscope (F.I.M.). The image has been shown by Tsong and Müller^(180,181) to distinguish between the different atoms in each plane and detect the occurrence of ordering in the Pt/Co alloy system. Platinum atoms were found to image while the cobalt did not.

The variation of the electronic structure of many disordered alloys in the Cu/Pt system have been studied by Ohshima and Watanabe⁽¹⁸²⁾ who have shown the validity of using forward and back diffracted electrons in an electron microscope.

Anderson, Conn and Brandenberger⁽¹⁸³⁾ carried out a study of silica supported platinum copper alloys and found increasing surface enrichment of copper when the crystallite size was increased.

Crystallites of less than 30Å diameter had a surface composition similar to that of the interior. However, Hardy and Linnett⁽¹⁸⁴⁾ did not detect surface segregation in palladium/silver or copper/nickel alloys using the deeper surface techniques of electron probe.

Using the high surface sensitivity of A.E.S. Quinto, Sundaram and Robertson⁽¹³⁷⁾ have confirmed the lack of surface segregation in copper/nickel alloys. They observed preferential sputtering of copper from the surface layers.

In the platinum/tin alloy system Bouwman and Biloen⁽¹⁸⁵⁾ used a combination of A.E.S. and X.P.S. to fix the depth distribution of the alloy components. The different energies

of the characteristic electrons detected in each method were associated with different escape depths through the outer surface atomic layers. Using a block step model they found tin enrichment in a surface layer ~ 3 M-L thick in PtSn and ~ 5 M-L in Pt_3Sn . The enrichment was matched by a depleted volume further into the alloy surface. Similarly, Williams and Boudart⁽¹⁸⁶⁾ have found extensive concentration of gold above its bulk concentration in nickel. This segregation was greatly reduced by adsorption of oxygen on the alloy surface. They point out that surface segregation studied by A.E.S. is most clearly seen if Auger transitions are chosen at the energy giving shortest mean free path for the electrons of that material.

Surface alloying in the copper on tungsten(110) system was detected by Taylor⁽¹⁸⁷⁾. On a cleaned W(110) surface epitaxial growth with single axis pseudomorphic constraint was seen at 0.5 M-L coverage. This superlattice corresponded to 7 mesh units long. Complex spots, attributable to multiple scattering were observed in the coverage range 1-3 M-L. Adsorption of copper on a half coverage oxygen structure on the tungsten proceeded as island growth. Oxygen was found to give pre-adsorbed copper mobility to change structure.

I.3.3 Epitaxy and Pseudomorphism in Surface Films

The properties of film growth have been extensively studied in many systems. The occurrence of epitaxial growth, in which the crystallographic orientation of an overlayer is simply related to that of the substrate, has been the subject of many theories. Pseudomorphism is a special case of

epitaxy in which the growth of the overlayer material exactly mimicks the atomic arrangement of the substrate.

The various growth modes for deposited films are reviewed by Bauer and Poppa⁽¹⁸⁸⁾. The basic growth mechanisms differ for changing film/substrate pairs. Where the surface energy of the adatoms is large compared with the substrate there will be a strong tendency to form low coverage islands with little reference to the substrate orientation. When a film of similar surface energy to the substrate is deposited there will be a limited depth of pseudomorphic growth. For high strain energy in the film the mismatch encourages a rapid growth of island structures. Where surface film strain is low and only a small misfit exists between adsorbate and substrate mesh dimensions a strained film may grow pseudomorphically for many atomic layers. This theory, proposed by Frank and van der Merwe, is expanded with a review of other theories by van der Merwe⁽¹⁸⁹⁾.

Evidence of pseudomorphism has been presented by Matthews and Jesser⁽¹⁹⁰⁾ for platinum evaporated onto gold so that a wedge film was formed. When studied by Transmission Electron Microscopy (T.E.M.) the 2-10 Å film areas were strained to match the gold surface but greater thickness films developed dislocations to relieve the stress. This surface behaviour is in accord with van der Merwe's theory.

CHAPTER II EXPERIMENTAL TECHNIQUES USED AND METHODS DEVELOPED.

II.1 Low Energy Electron Diffraction

II.1.1 LEED/A.E.S. Vacuum System.

The basic system, a commercial unit supplied by Vacuum Generators Ltd., was taken over from A. Owens who had been studying gas adsorption on the (110) face of nickel. He has already described the characteristics of the LEED optics and performance of the vacuum system. The LEED system was normally operated in the Field Free mode by maintaining the first grid nearest to the crystal at earth potential so that electrons diffracted from the crystal were unaffected by electro-static fields. A small trimming magnet was used to counteract stray magnetic fields from the sputter ion pumps, magnetic system parts, and the earth's field. The middle grid was maintained at a potential within 5 V of the LEED gun cathode so that uniform minimum background intensity was observed on the fluorescent screen. In this 3 grid system the final grid adjacent to the screen was maintained at earth potential to reduce field penetration distortion at the middle electron energy selecting grid from the high potential on the screen (~5 kV).

Diffraction patterns observed in the system could be recorded by photographing with a Praktica AB single lens reflex camera with an additional 2 diopetre close up lens. Exposure times of 5-10 minutes were required to record weak

patterns on Ilford HP4 film. This time was ~ 4 times greater than that reported by Owens for similar electron gun conditions indicating that the fluorescent screen had become less efficient due to film evaporation from the nickel crystal and holder. Exposure times were reduced to 1 min. with no noticeable loss of quality by using Kodak 2495 RAR film developed in Ilford "D8".

II.1.2 LEED - Screen Constants

The normal method of use of a LEED system for surface mesh dimension determination requires a knowledge of beam energy, screen radius of curvature and screen aperture diameter. With a crystal at the screen centre of curvature the first order diffraction spots from a group of planes intersect the edge of the screen when

$$\sin \Theta = \lambda/d = r_c/r_a$$

r_c is screen radius of curvature

r_a is screen aperture radius

d is interplanar spacing (Å)

λ is electron wavelength = $\sqrt{150.4/V}$

V is the electron ~~electron~~ energy (i.e. accelerating voltage).

If the dimensions supplied by the manufacturers of the LEED system are used to determine the surface mesh of nickel from the patterns of Owens⁽²⁵⁾ e.g. Figure III.36 where the Ni(110) (11) first order beams are on the edge of the screen at 73 V

$$\text{Then } \sin \Theta \text{ (full screen)} = 2.05/2.60$$

$$d_{(11)} = \frac{2.60}{2.05} \sqrt{\frac{150.4}{73}}$$

The nearest neighbour distance in nickel, $d_{(10)}$, is $\sqrt{2/3} d_{(11)}$

Then $d_{(10)} = 1.49 \text{ \AA}$.

As there have been no reports of such a deviation from the bulk spacing of $2.49 \text{ \AA}$ the system errors have been investigated to enable surface spacing measurements to be made.

The following relevant parameters were measured to detect the source of error.

The grid and screen dimensions were found to match the manufacturer's figures when disassembled. However, the useful area of phosphor could not be measured under these conditions.

A method was developed to ensure that the crystal was positioned within 1 mm of the centre of curvature for LEED and A.E.S. and is described in section III.5.2.1.

The electron accelerating potential was measured with a digital volt meter (D.V.M.) and was found to be within 1 V of that indicated in the range 0-100 V.

Alternatively, taking the clean Ni(110) diffraction pattern as resulting from a rectangular surface mesh of dimensions $a = 2.49 \text{ \AA}$ and $b = 3.52 \text{ \AA}$, the effective LEED screen aperture for diffraction spots visible at its edge was 93.2 mm. When, for the work described here, the nickel crystal was replaced by platinum crystals the calibration of useful screen aperture was found to be within 2% of this value.

II.2 Auger Electron Spectroscopy

The system was a standard 3 grid retarding field analyser supplied by Vacuum Generators Ltd. as an extension to the LEED system and used the LEED grids and screen for energy selection. The detailed circuits and operating instructions are listed in V.G. Technical Information Bulletins 01.721 to 01.729. The system as supplied was only capable of operating at a low resolution ($\sim 2.5\%$) which was limited by the field penetration at the middle (energy selection) grid.

II.2.1 The Incident Electron Beam

The exciting electron beam was obtained from a L.E.G. 3 glancing incidence gun positioned in a side arm of the system, the axis of which was at 78° to the LEED gun axis. The gun was supplied from a LED 3 Low Noise unit which stabilised the filament current and provided potentials for the two non-earthed electrodes. The normal operating conditions for quantitative work were:-

A4 Electrode (Beam Energy)	2.5 kV
A2 Electrode (Focussing)	620 V
Filament emission (to can)	0.94 mA
Filament current - to maintain emission (~ 3.7 A)	

The beam could be deflected in the system by two pairs of electrostatic plates fed from a battery supply, or by manipulation of a trimming magnet. However, movement of the magnet could change the field between the crystal and the grid and so deflect Auger electrons from a straight line

radial path to the screen when maximum resolution was obtained. A magnet position was found where resolution was best and all further incident beam moves were carried out using the electrostatic plates.

The incident beam was found to be responsible for much of the noise in the Auger spectrum. The current control potentiometer was replaced when necessary when violent current changes occurred. Spurious Auger peaks were observed when scanning the energy range 400 - 1000 eV where maximum sensitivity was required to detect transitions. When the energy ramp was stopped the signal variation continued, unlike a true Auger feature, indicating a change of screen current. This change in current was eventually correlated with the passing of the heavy iron counterweight of a nearby lift. Small movements of the beam on the sample caused most noise when the beam was positioned near the edge of a single crystal or at a low angle of incidence on rough or polycrystalline samples.

The electron beam current is an important parameter in the quantitative use of A.E.S. as the output signal is directly proportional to it. The most satisfactory method is by the use of a Faraday cup, which may be interchanged with the sample, designed to trap all incident electrons. The current that may be measured in the earthing line of the crystal (I_c) is related to the beam current (I_p) by:

$$I_c = I_p - I_s$$

At the primary beam energy used in this work the secondary current (I_s) was approximately twice the primary current,

resulting in a net electron flow from earth to the crystal. As the secondary electron coefficient varied considerably with surface cleanliness, roughness and beam angle of incidence the earth current was a poor measure of constant primary beam current.

If the crystal was positively biased the secondary current was reduced as many of the electrons could not climb the potential gradient to the system walls and grids. The characteristics of this secondary current are shown in Figure II.1. Although the collected current was still increasing slowly at 500 V bias this was probably largely due to collection of secondary electrons created in the gun and not in the primary beam. A bias of 500 V was used as the standard for primary beam current measurement. The standard emission of 0.94 mA corresponded to a beam current of $60^{+1} \mu\text{A}$ for a normally activated filament.

II.2.2 The Retarding Field Analyser

The 3-grid LEED optics were operated as a retarding field analyser. The first grid was held at earth potential to preserve the field free region from the crystal to the analyser. The energy gating occurred at the second grid which was slowly ramped through the range of energies of interest. Only electrons having energy above the gate potential passed through the grid to reach the fluorescent screen which should have been biased to collect them. To enable a.c. amplification followed by synchronous detection methods to be used the third grid between the gate and the screen was earthed. This reduced the capacitance between the gate,

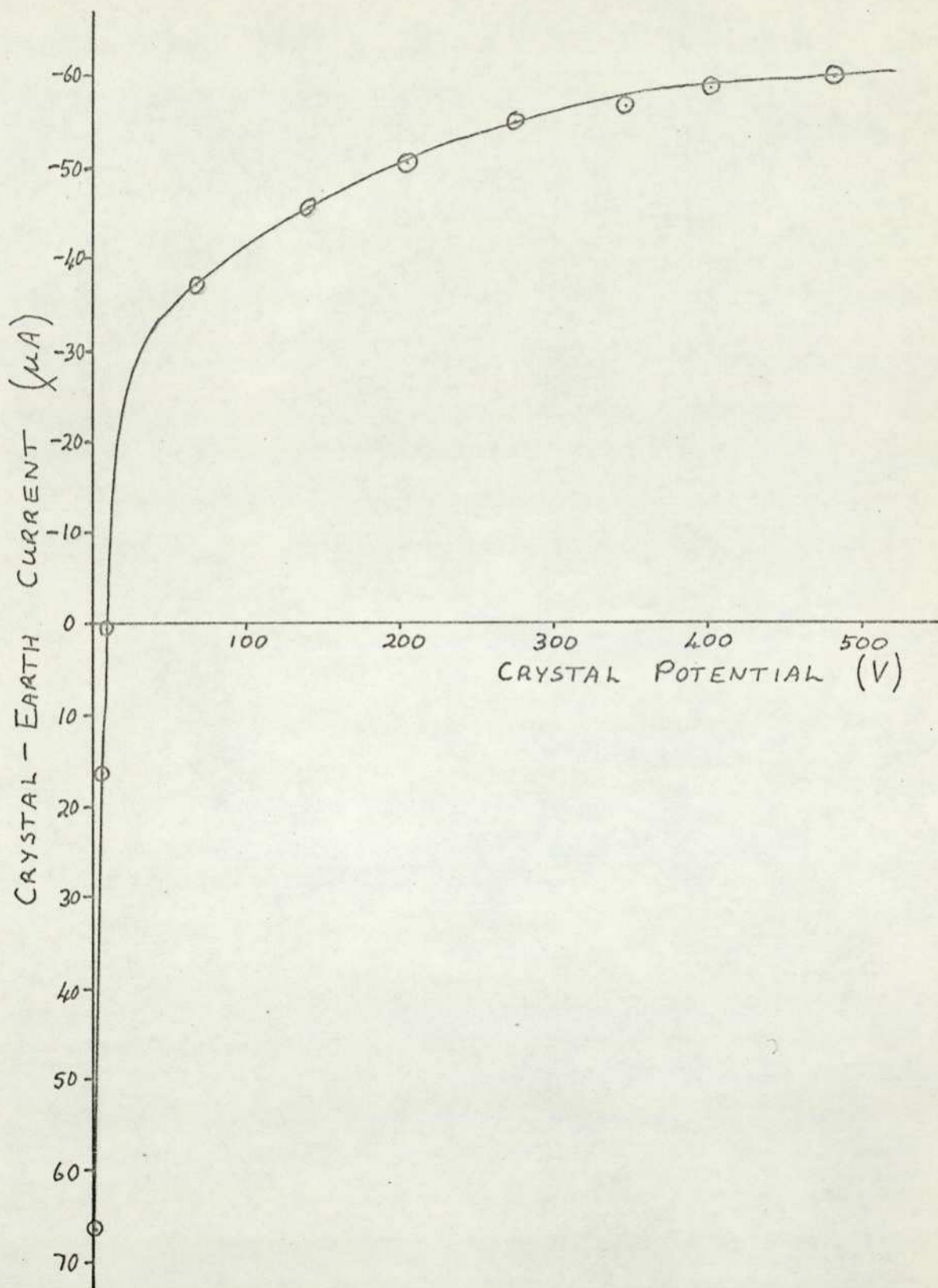


FIGURE II.1 The current from crystal to earth at different crystal potentials. (Filament at -2.5 kV)

where a small a.c. modulation signal was superimposed on the gate d.c. level, and the collector, where the a.c. component of the electron current was detected in a tuned circuit. The small remaining capacitance between gate and collector was sufficient to cause overloading of the amplifiers if a capacitance neutralising bridge was not used. The V.G. de Sauty bridge fed an equal signal to the non-screen end of the detection transformer so that currents in the transformer were solely due to the a.c. component of the electron current.

The major cause of low resolution in this system, field penetration at the gate grid, was determined by measuring the gate potential at which a beam of electrons of known maximum energy could be first detected at the collector. The electron beam from the normal incidence (LEED) gun was directed at a Pt(100) crystal at the system centre of curvature. The current reaching the screen biased at +210 V was measured with a Keithly Pico-ammeter. The beam energy was set at 1000 V and with the 2 grids next to the screen connected together the gate grid voltage was slowly reduced from 1100 V until the current detected by the Pico-ammeter rose sharply from its low leakage value. The first and third grids were then connected together at earth potential and the ramping repeated on the gate grid. The appearance of the elastic electron peak occurred at a higher energy and rose less sharply with voltage change. These results are plotted in Figure II.2.

This penetration characteristic was similar to that

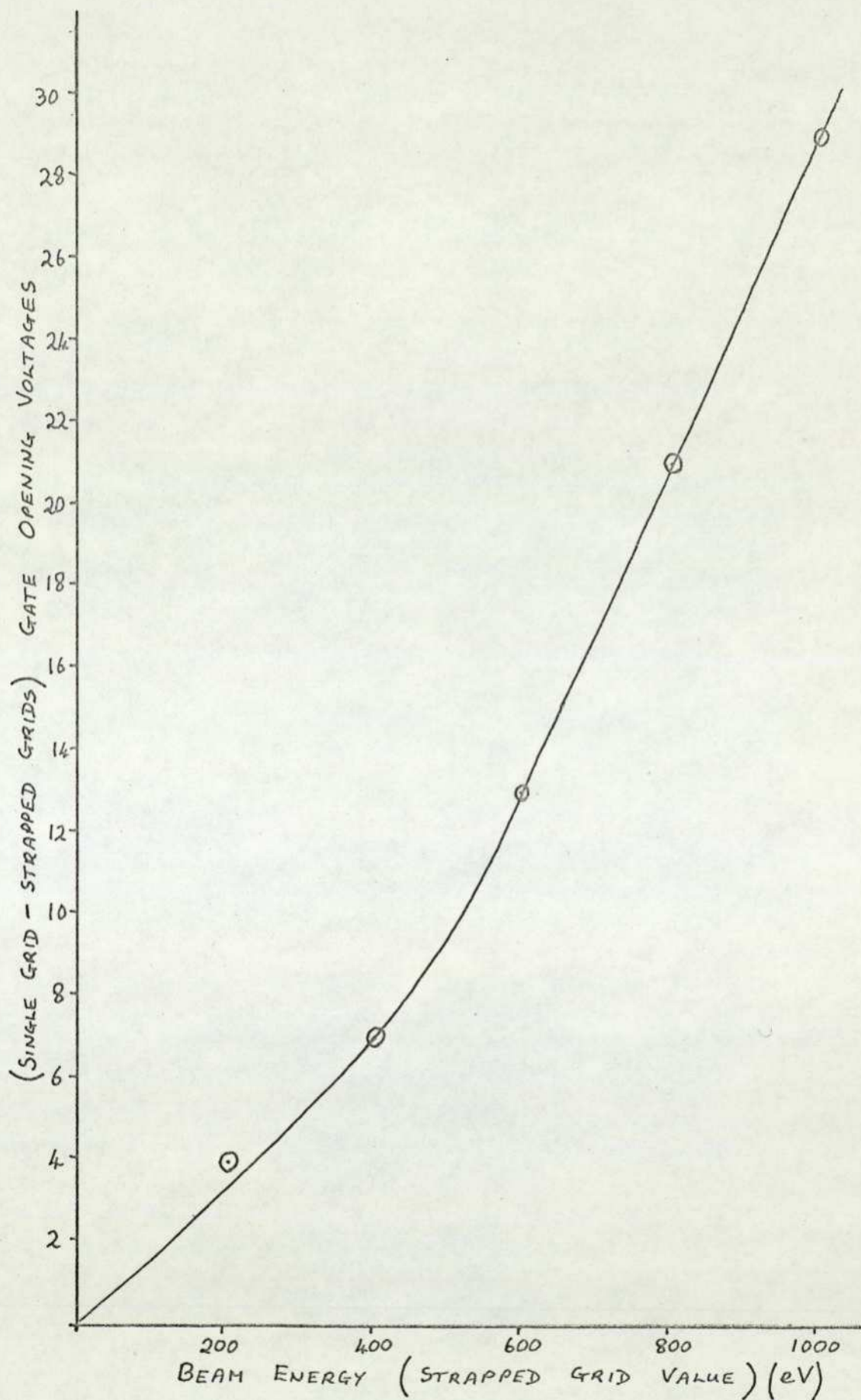


FIGURE II.2 Field penetration through a single grid
(Relative to 2 strapped grids)

determined by Taylor⁽¹⁹¹⁾ for a 3 grid system.

The point at which a feature was observed in the electron distribution or derivative spectrum was labelled by reference to the potential on the gating grid. This point could not be directly related to observations on a different instrument without reference to the cut off characteristic for the grid or analyser system used. Peaks recorded at 1030 eV on this system would appear at 1000 eV on an otherwise similar 4 grid system.

A retarding field analyser carries out selection of the component of the electron momentum normal to the plane of the grids. In the LEED optics system the electrons should be travelling radially from the crystal through the spherical grids to the screen. If the crystal is not positioned at the centre of curvature, or the system has a significant magnetic or electrostatic field the electrons will be deflected from the radial course. In this event the electrons will be stopped at a lower grid potential than for a radial path. Such effects must have counteracted to some extent the true field penetration recorded in Figure II.2.

II.2.3 Gate Grid Modulation

The modulator of the V.G. Auger system was found to be uncalibrated and non-linear. To enable the best choice of modulation to be selected to give a compromise between peak size and resolution the grid modulation was recorded on an oscilloscope to calibrate dial readings. This is shown in Figure II.3 after correction for oscilloscope calibration error.

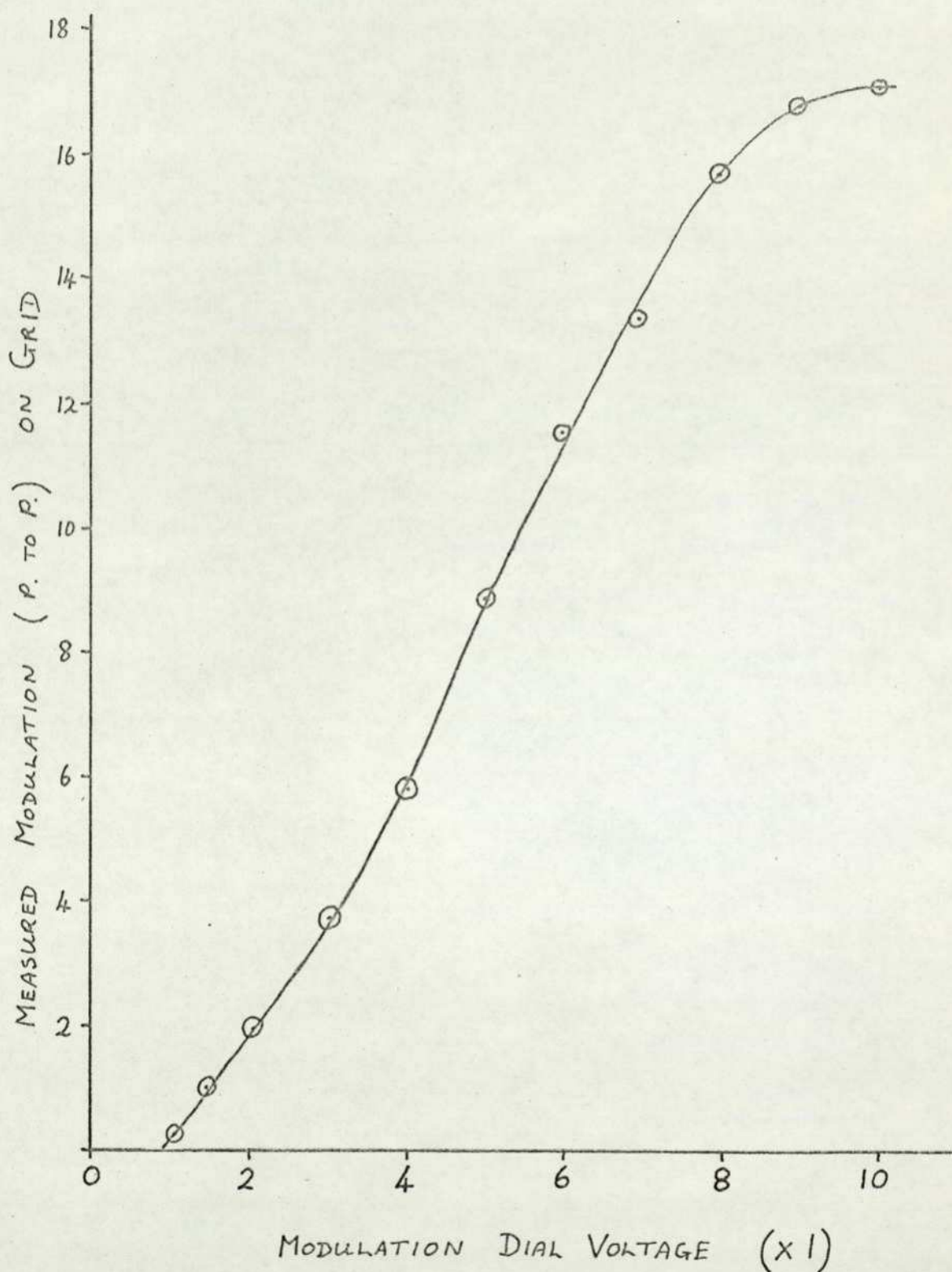


FIGURE II.3 Calibration of Instrument Modulation Dial.

The gate grid modulation was used as the main control parameter to enable Auger peaks of inherently differing sizes to be recorded and displayed together. Peaks in the range 30-300 eV were based on a rapidly varying background but both peaks and background were suitably reduced by smaller modulation levels. An optimum modulation level was chosen for each Auger transition and this was used for most work. When it became necessary to modify this level spectra were recorded at both the normal and the new level to provide a correction factor.

II.2.4 The Screen/Collector

The fluorescent LEED screen acted as the electron collector in the Auger mode. The standard system provided a control which apparently biased the screen in the range 0 to +250 V. This power unit supplied the screen through a 10 M Ω fixed resistor so that for screen currents of 25 μ A even maximum bias voltage produced no resultant screen attractive potential. Reduction of the screen feed resistor to 2.5 M Ω improved Auger signals below 250 eV by $\sim$ 100%.

II.2.5 Signal Amplification and Detection

Improvements in the signal/noise ratio of both energy distribution curves $N(E)/E$ and the first derivative curves $dN(E)/E$ were obtained by removing earth loops improving signal screening and replacement of poor quality components, particularly the main amplifier gain skeleton potentiometer. The amplifier damping control was increased by increasing the Bandwidth 2 setting to 5 secs. time constant. 0.5 sec or 2 sec time constants could alternatively be used.

II.2.6 Operation of 3 Grid Retarding Field Analyser at High Resolution

The standard resolution of $\sim 2.5\%$ used for much of the work was adequate for simple Auger spectra. However, when peak enhancement was suspected due to chemical modifications to the electron energy positions and distributions a higher resolution was required. The standard system had a resolution of 3 V when the gate was held at 120 V. By slowing higher energy Auger electrons to this energy before analysis the 3 V resolution could be applied to the copper Auger peaks in the 700-950 eV range. To accomplish the energy reduction the crystal potential was raised above earth so that the emitted Auger electrons in the secondary electron spectrum were slowed down by the potential gradient on their path to the first grid of the retarding field analyser. To enable a range of energies to be scanned the crystal potential was varied while the gate grid was held at -120 V with an applied modulation as usual. The effective gate energy (E_g) was then

$$E_g = \text{Crystal} - \text{Gate Grid Voltage}$$

(observing polarity)

The E.H.T. ramp generator supplied for the A.E.S. system could not be used to supply the scanning crystal potential as it was designed to provide negative voltages only. However, to provide a variable positive potential a battery pack was made up to provide ≤ 1000 V with the negative terminal connected to the ramp generator output. The potential on the positive terminal of the battery pack then became Ramp output (-) + 1000 V. This simple idea could not be used

directly in practice as the ramp generator circuit was effectively a variable voltage source with a diode in the output. The ramp control operated only as long as the diode passed forward current. If an excess of electrons was attracted to the crystal, by the positive potential, the output terminal of the ramp unit dropped out of control until it matched the battery potential. To allow the ramp unit to control the final crystal potential a 5 M Ω resistor was shorted across the ramp unit output so that a small current was drawn from it to regain control. The battery pack was made up with 5 K Ω resistors between each 67 V battery to reduce the danger of electric shock. A method was devised so that the battery packs could be connected in a sequence so that only terminals on the "earthy" side of the system would be touched. This has been notified to the following user of the equipment.

High resolution spectra, with an energy resolution of between 0.45 and 0.3 μ are shown in section III.5.2.6. The choice of 120 V as gating grid potential was a compromise between good resolution at a low potential and sufficient screening of low energy secondary electrons from all parts of the system.

In the high resolution mode care was required in choosing the grid modulation voltage to avoid degradation of the resolution. Resolution was entirely grid limited above 300 V in the low resolution mode. However, the improved signal to noise ratio found at higher resolution enabled 5 V peak to peak modulation to be used without serious

modification of the copper high energy spectrum.

II.3 Radio Frequency Heating Methods

Induced current sample heating was adopted to avoid the contamination inherently caused in the use of any other methods. In this method circulating currents are induced in a conducting material in the rapidly varying magnetic field near a coil carrying high frequency current. It is particularly effective in a vacuum system where sample heat loss is restricted to radiation and conduction along small size support wires and thermocouple leads. The power dissipated in the sample may be moderate even at high temperatures:-

$$\text{Heat Loss by Radiation} = 5.67 \text{ E } 10^{-12} (T_2^4 - T_1^4) \text{ W cm}^{-2}$$

(from Stefan - Boltzman law of radiation)

where E = Emissivity (0.05 for platinum)

T_1 = Ambient Temperature ($^{\circ}\text{K}$)

T_2 = Sample Temperature ($^{\circ}\text{K}$)

Applying this to a 1 cm disc of platinum heated to 1000°C in a room temperature system:-

$$\text{Rate of heat loss by radiation} = 1.2 \text{ W.}$$

II.3.1 Practical Considerations

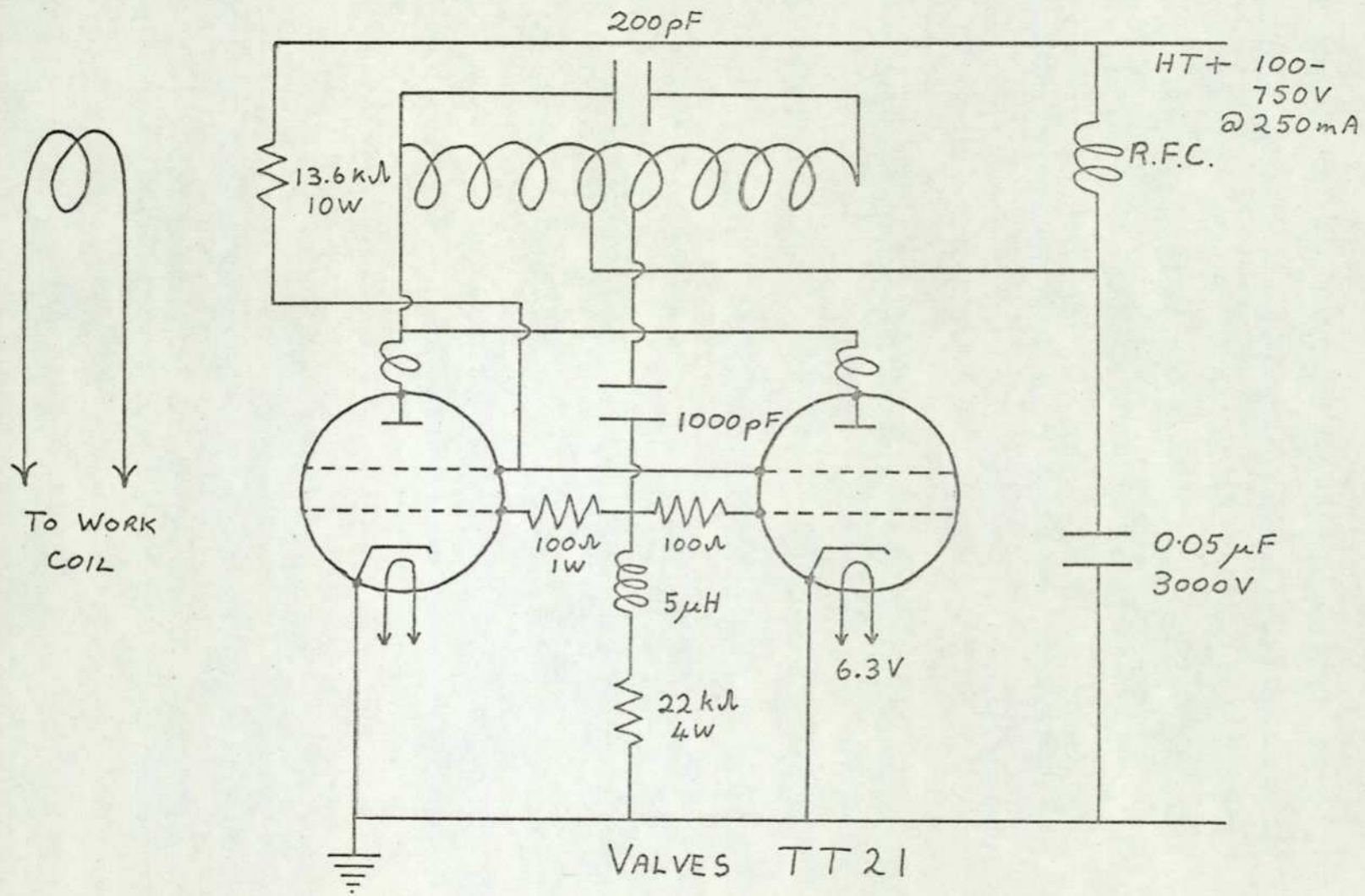
High frequency induction heating is used extensively in industrial processes and is well documented on that scale (e.g. 192-5). No commercial equipment or circuits were found for a unit which could induce a power of a few Watts into the LEED/Auger samples. An attempt was made to pass

rapidly changing currents through a copper work coil by sequentially discharging large capacitors through thyristors triggered from a free running oscillator. Although the thyristor switch-on time was sufficiently fast (0.1 ms) the long recovery time before it could be again switched allowed a maximum repetition rate of 400 pulses per sec. This rate was too low to induce significant heating effect.

A more conventional R-F generator was built as a scaled-down version of industrial units. The common Colpitts oscillator could not be built as such a design required a range of capacitors which could not be obtained. However a Hartley-type circuit could be tuned by easily constructed coils. The working circuit is shown in Figure II.4 and has two TT21 transmitting valves running in parallel. Further valves may be added for higher power if antiparasitic chokes are fitted in the anode circuit. The tank-coil was an air-spaced 16 turn, 60 mm diameter spiral of 18 s.w.g. wire with a power extracting loop of 7 turns of 70 mm diameter concentric with it. This unit was built in a screened box with a cooling fan to prevent overheating of the valves or coils. Power was obtained from an A.P.T. Electronic Industries Ltd. Model 513 Regulated Power Supply which produced up to 750 mA at 750 V. The operating frequency was ~4 MHz.

To enable the power unit to be positioned at least 1 m from the vacuum system a tuning head was built. When tuned for maximum power extraction the grid current dipped. The R.F. current flowing into the vacuum system load coil

FIGURE 1.4 R.F. Heating Oscillator.



was indicated on a shunted 0 - 10 A thermo-ammeter. Stable oscillation of the generator occurred at supply voltages in the range 100 - 750 V; the output power was continuously variable in this range.

Many designs of work coil were tried in the system. Maximum coupling with the sample occurred when the sample to coil separation was very small, but sufficient room was left to manoeuvre the sample in or out of the coil. The highest coupling to foil samples was obtained with a double spiral coil. However, the field induced by the outer coils of the spiral heated the inner coils to cause outgassing and possible evaporation.

All coils fed via a stainless steel conductor feed-through overheated in use even with water cooling coils on the outer ends. Low outgassing rates were obtained when a helical 16 s.w.g. molybdenum wire coil was fed from a high current copper conductor feedthrough with water cooled outer ends.

The overall efficiency of the system was low ($<1\%$) but thin samples with a total surface area of 200 mm^2 could be heated to 1100°C . A Comark multimeter which had been used for earlier thermocouple voltage measurement could not be used while the R-F generator was operating due to induced pick-up. To overcome this a Pye Scalamp Spot Galvanometer was fitted with a series resistor which was chosen to give a deflection of 1 large division per 1.0 mV as determined with a potentiometer. The thermocouple voltage could then be determined while the sample was R.F. heated.

The mass spectrometer, ion gauge and copper source and monitor were unaffected by the R.F. heater but LEED, argon ion bombardment and A.E.S. could not be used on a heated sample positioned in a work coil.

II.4 Argon Ion Bombardment

The standard argon ion gun fitted to the system, a V.G. -AGS 1, was found unsuitable for cleaning the platinum samples as the ion current density was low and the outgassing rate was high. The characteristics of this gun are given in Reference 25 with a recorded maximum current of 0.7 μ A measured at the crystal.

Argon glow discharge cleaning was investigated. Although in a static system the argon pressure required for a glow discharge was too high, ~ 1 torr, leading to ion pump instability on pump down, a flow system through a leak valve along a capillary tube caused a local high pressure at the sample. This also suppressed local glow discharges along the voltage feed wire to the sample and thermocouple leads.

The glow discharge occurring while flowing gas into the system through a capillary tube to the crystal and out to a sorption pump was generally unstable. It was found possible to set up a stable glow solely near the front face of a sample held at a potential of -350 V with respect to the nearby R.F. heating work coil. Typical operating conditions were 35 μ A current at 250 V.

The sputtering rate from a platinum sample was signif-

icant - a grey film was observed on a copper R.F. work coil near the sample after a 1 hour sputtering treatment. However the time taken for the system pressure to fall to $<1 \times 10^{-8}$ torr was more than 1 hour during which time new surface contamination was found to have occurred.

A modification to the method used for argon ion bombardment using the V.G.-AGS 1 gun improved the output by $\sim 100\%$ to $1.5 \mu\text{A}$ total. A 75 mm permanent bar magnet was supported outside the gun stainless steel tube so as to produce a local intense magnetic field in the ionising area of the gun. The increased electron path length in the field caused more ionising collisions and increased output. However the high degassing rate remained a problem for prolonged sputtering. The design faults in the gun responsible for the poor performance were :

- 1) the close proximity of a screening grid and outer can to the filament caused a large area of metal to be heated unnecessarily.
- 2) the grid volume in which useful ionisation occurred was small.
- 3) the extraction grid aperture was small with a fine mesh grid.

These features gave a directed beam in a field free system but in practice a bias on the sample was used to attract ions.

A new unit was built from a Varian Bayard-Alpert Ion Gauge on the same principles but with the housing tube acting as the outer screen and the large diameter grid

modified by removing the top cover grid. A coarse grid of stainless steel wire was positioned at the inner end of the housing tube to extract ions produced in the grid space. The focussing of extracted ions was very poor in a field free region but application of a negative bias of up to 450 V allowed efficient ion current collection.

This gun was operated from a standard control box which provided a stable 5 mA emission from the tungsten filament held at -220 V below the grid. As the filament potential could be raised by up to +300 V above earth the ions leaving the extractor grid were of between 220 and 520 eV energy.

With -200 V on the crystal a maximum ion current was detected with a grid potential of 240 V above earth. The variation of ion current with pressure is shown in Figure II.5 and indicates that the highest pressure consistent with a sufficiently fast pump down should be used. The output from this gun was particularly enhanced by positioning a small bar magnet to give a field in the grid space and this produced an ion current of 10-15 uA at the crystal biased at -450 V.

The outgassing rate of this gun when operating was minimal, and did not raise the ultimate pumped pressure by more than 2×10^{-10} torr. As with all measurements of argon ion currents it was difficult to determine the proportion of the current striking the sample relative to that reaching supply leads which were at the same potential. However, the sample was the nearest target to the gun.

This gun was found to efficiently clean the platinum

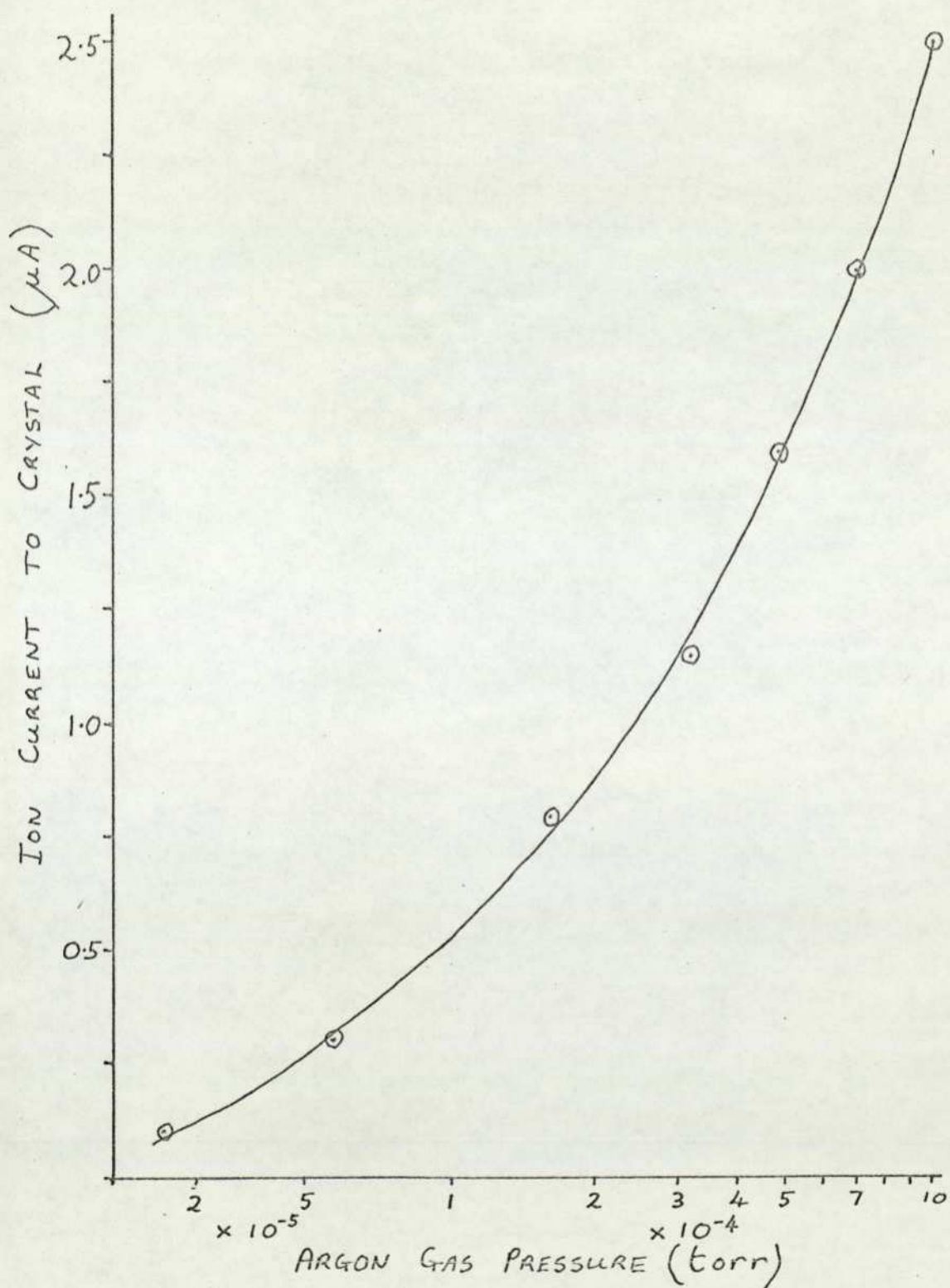


FIGURE II.5 Variation of Ion Gun Current with Pressure (No Magnetic Field).

samples; in particular, it removed all surface oxygen detected by A.E.S. resulting from oxygen treatments to remove sulphur and carbon in a 30 min. bombardment at 5-10 μ A.

II.5 Evaporation Sources

II.5.1 Tungsten 'Hairpin' Sources

All gold films and many copper films were prepared by evaporation from a single (0.010") wire of tungsten heated by a current of 3.5 - 4.5 A. This wire was connected to two terminals of a 3-way U.H.V. current feedthrough fitted in a cross piece on a side flange of the LEED system. When the source was installed the line of sight through the end of the cross piece could be checked from the tip of the hairpin, through the collimating disc to the R.F. coil in which the substrate was positioned for coating. This sight line was also used to determine the shutter size and position required to prevent evaporated metal reaching the LEED fluorescent screen.

The tungsten wire source was identical when viewed from either side of plane of the wire and so evaporated metal symmetrically about the plane. When this source was fitted in the cross piece the metal flux to the crystal was indirectly monitored by the quartz crystal positioned in the opposite direction to that to the crystal, as shown in Figure II.6.

When the vacuum system was pumped and after baking, the wire gave rise to an initial pressure pulse when heated with

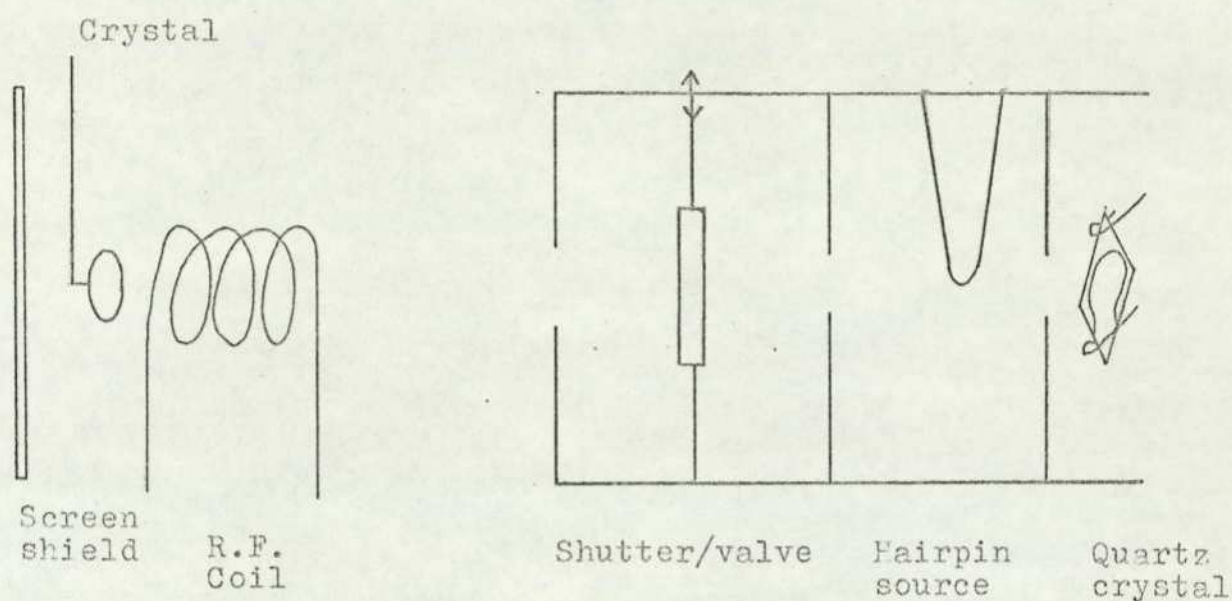


FIGURE II.6 Experimental arrangement for evaporation from a hairpin source.

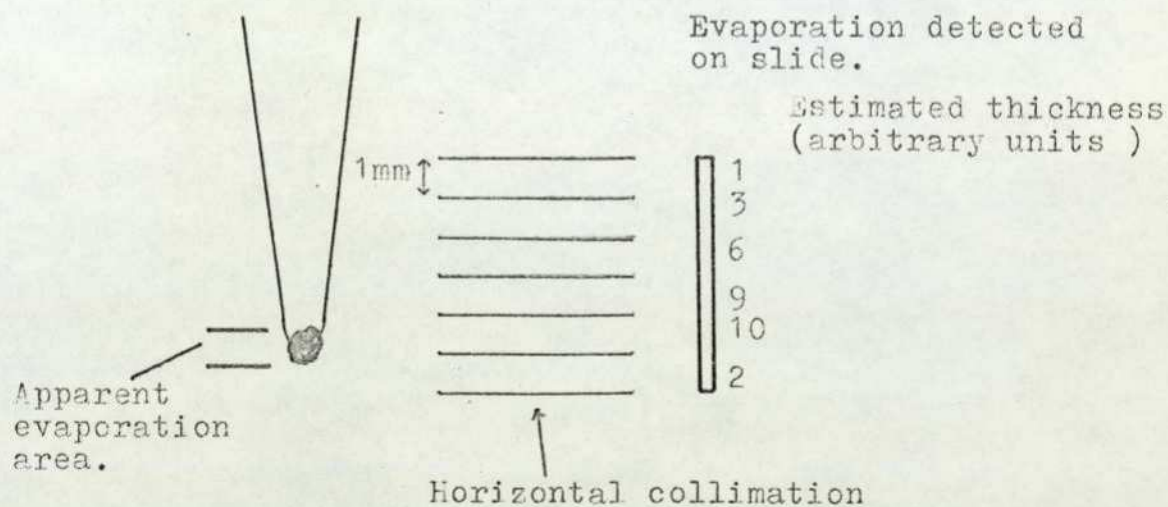


FIGURE II.7 Evaporation from a hairpin source.

the degas current of 3 A but after an initial evaporation against the shutter the subsequent evaporations were carried out at a system pressure rising to $<2 \times 10^{-9}$ torr; most of this gas being carbon monoxide.

Evaporation from a hairpin source appeared to be from the molten drop of metal, which, due to its small size (~ 1.5 mm), was taken as a point source for calibration purposes. An experiment to determine the evaporation characteristics of a hairpin source was set up as in Figure II.7. The evaporation from the wire was collimated horizontally so that each plated section on the glass slide was due to evaporation from the corresponding 1 mm vertical section of the wire hairpin. The estimated relative thicknesses for copper evaporated at a current of 4 A are shown in the Figure and explain the discrepancies between anticipated film thickness at the crystal and that measured by Atomic Absorption. The proportion of the metal evaporated within ± 1.5 mm of the tip of the wire was less than 70%. For the evaporations from this source which were not carried out with restricting shields the crystal monitor was exposed to a flux from a larger source than was the sample substrate. The initial calibration, which depended on the film thickness on the glass slide, quartz crystal and platinum sample being related only by $(\text{distance})^{-2}$, predicted film thicknesses at least 40% greater than those deposited. However, the evaporation rate, as determined by the quartz crystal monitor, was found to be constant at fixed current through the wire irrespective of the size of the evaporant metal drop. The

evaporation rate was thus dependent on the power dissipated in the wire and not the supply of metal and so the source, operated under standard conditions, was expected to have a constant error from the calibration.

This error was eliminated by positioning shields on either side of the wire so that only 1.5 mm of the tip of the wire was effective for evaporation to the monitor.

The evaporation rate for this source measured on the sample crystal was normally maintained at 0.003 monolayers (M-L) of copper per second.

The wire source was limited to small charges of evaporant metal which produced very thin films on the crystal due to larger separation between source and sample; the reloading process was time consuming and disruptive. Various schemes were devised whereby the hairpin could be reloaded under vacuum. The method shown in Figure II.8 allowed 5 reloading charges to be held by a second wire run to the third available terminal. The charges could only be released in order on passing a current through wire 2 as the charges shorted the two wires together, reducing the heating on the inner charges. As the hook on the charge was melted the charge was released to drop to the tip and caused a sudden drop in current in wire 2 as its resistance increased. The technique was not sufficiently reliable for continued use.

II.5.2 Tantalum Can Source

A successful high capacity can source was developed to overcome the need for frequent reloading as required by

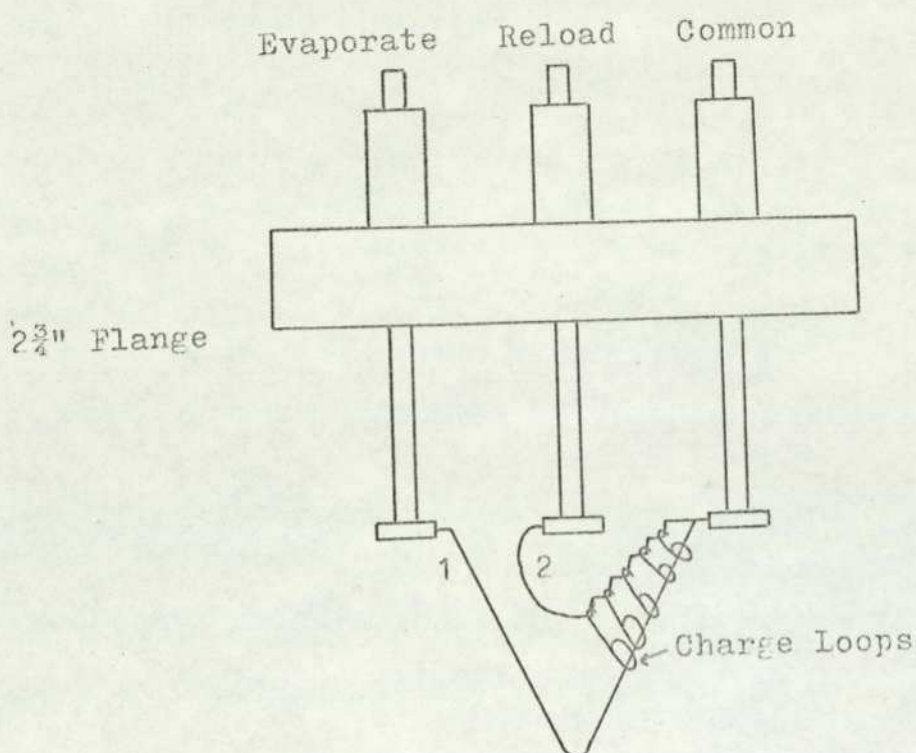


FIGURE II.8

Multiple Charge Evaporation Source.

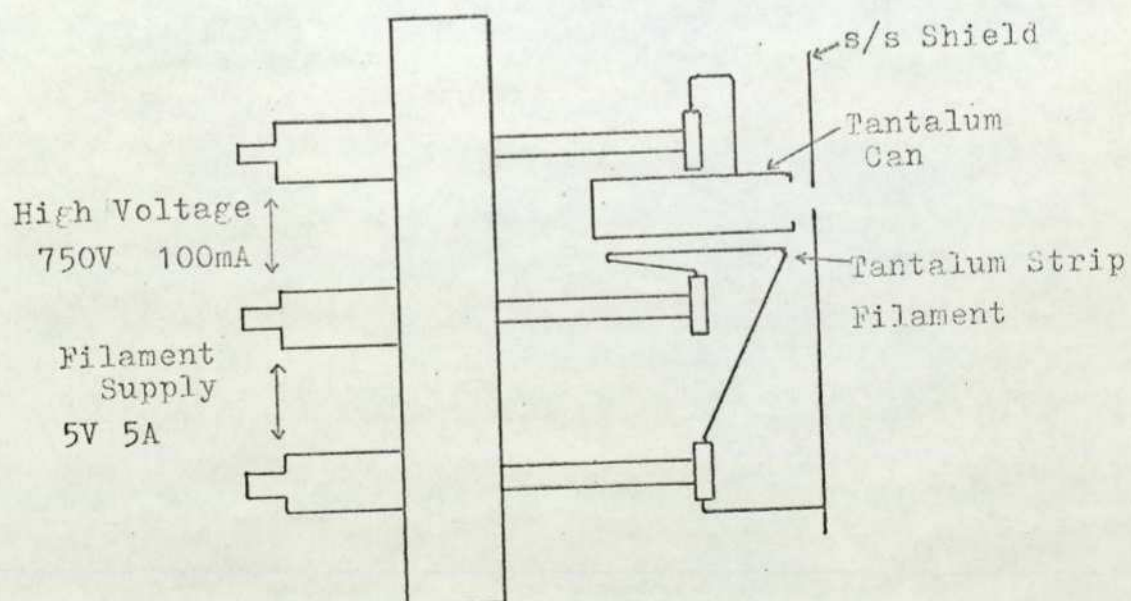


FIGURE II.9

Tantalum Can Source.

the wire sources. The unit is shown in Figure II.9. The tantalum foil filament was heated by passing a current of ~ 5 A while the can was maintained at +750 V with respect to earth. The filament current was finely adjusted to maintain an emission of 100 mA to the can when the vapour from the liquid copper in the can deposited on the platinum sample at a rate of ~ 0.1 M-L sec^{-1} of bulk copper. This source evaporated from the end of the can through collimating apertures into the LEED chamber. The quartz crystal monitoring was rearranged so that a 10° off axis portion of the beam to the platinum sample struck the quartz crystal of the monitor through a second hole in a collimating plate.

The can source, with its large mass and high power dissipation (80 W), caused the LEED system pressure to rise to 2×10^{-7} torr during the first evaporation after reloading. This reduced to 5×10^{-8} torr on subsequent evaporation with carbon monoxide as the major component of the released gas.

II.6 Quartz Crystal Deposition Monitors

II.6.1 Design of Monitors

Two types of quartz crystal monitor were constructed; the first responded to the backward flux from the tungsten wire source, the crystal being fitted on an 8-way low current feedthrough on the back of the cross piece attachment to the LEED system. In the second type the crystal was supported in the cross piece part of the LEED system to receive

10⁰ off-axis flux from the can source.

The quartz crystals used in these monitors and calibrated for this work were purchased in sets of 6 or 8, the crystals apparently being identical within each set.

Manufacturer	Fundamental Frequency
Marconi	10.9155 MHz
Marconi	11.7566
GEC	9.43055

All crystals were supplied in glass valve envelopes with B7G bases. The electrodes were circular discs of evaporated gold with metal lands to connections at diagonally opposite corners. At the points of connection the film was continued on the opposite side of the crystal to discourage oscillation at those points.

The sample crystals were taken from their glass envelopes and the soldered connectors removed. The solder remaining was removed by scraping with a razor blade. New connections were made around the gold lands with crook shaped 0.5 mm annealed gold wires gripping the crystal. These wires were then spot welded to the U.H.V. feedthroughs on a 2 $\frac{3}{4}$ " copper gasket flange. A shield plate was supported in front of the crystal to restrict the area of the crystal exposed to copper and heat.

The most suitable size of the aperture in this shield relative to the electrode size is, as described by King and Hoffman⁽¹⁹⁶⁾, a compromise between a large area with a greater sensitivity to film thickness and better linearity of response, and a small area with reduced thermal drift during

evaporation. For the earlier monitors the aperture was $3/16$ " as recommended by a commercial gauge manual. The electrode surface was exposed to an aluminium source through a $1/4$ " aperture prior to the first copper film deposition to enable heavy deposits of metal to be etched off. Etching was carried out with a strong ferric chloride solution and enabled each crystal to be used for many evaporations. The etchant was applied with a fine paint brush and agitated for several minutes before being washed off with distilled water. This could normally be carried out without removing the crystal from the clamping/connecting gold wires.

The drive for the crystal was derived from a single transistor circuit. The output signal from this oscillator was buffered with an emitter follower and could then be monitored with an oscilloscope. For accurate frequency determination a counter was employed but the high frequency crystal, employed to give sufficient sensitivity, oscillated beyond the range of a Racal Frequency Counter (Type SA535B). As only frequency changes were required an identical circuit was built, controlled by a similar crystal and the two oscillator outputs mixed and the beat frequency displayed on the counter. This system ensured that the sample crystal frequency changes due to voltage or temperature variations in the circuits were matched by the standard circuit. The only significant source of error in the beat frequency change was that due to unequal heating of the crystals.

The temperature/frequency characteristic of the GEC quartz crystal was measured to enable the importance of

temperature stability to be determined and to estimate the temperature rise of the plate during evaporation. The sealed sample crystal was partly immersed in a water bath and the standard crystal left at ambient temperature ($24^{\circ}\pm 1$) while the water bath temperature was varied. Moisture build-up on the connections to the glass envelope was minimised by screening, as this capacitance effect could shift the frequency considerably. The characteristic is plotted in Figure II.10 and shows that the frequency shift of the standard crystal due to a 1°C temperature change from a 22°C ambient was 5 Hz ($0.5 \text{ ppm deg. C}^{-1}$).

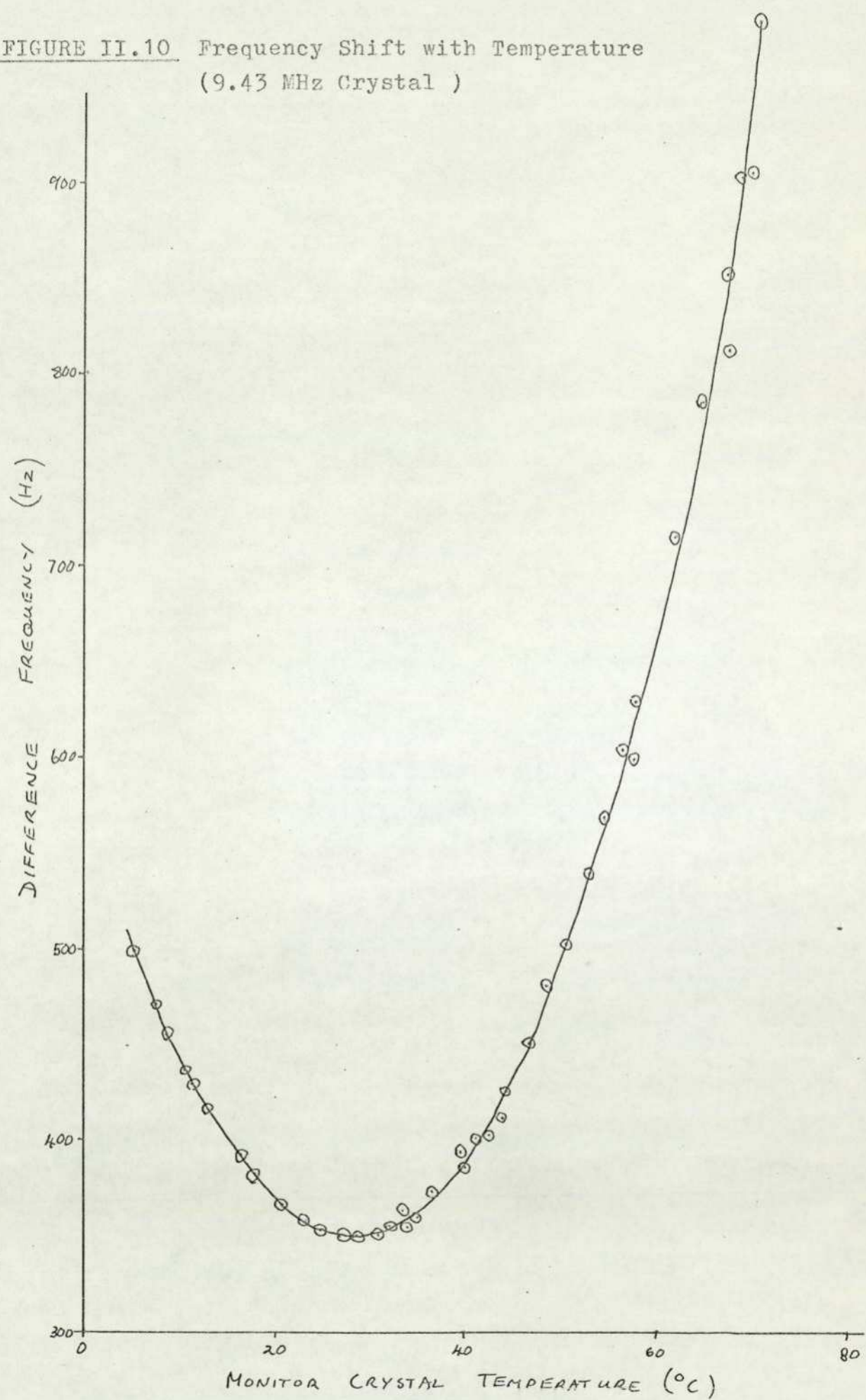
The frequency shift due to heating the sample crystal by radiant heat and condensation of the metal vapour depended on evaporation time. The normal evaporation rate from the can source of 0.1 M-L/sec of copper at the platinum crystal gave a frequency shift which dropped by ~ 10 Hz within the 5 mins after a 1 M-L film deposition, indicating that the crystal temperature had not exceeded 40°C during evaporation. The slower evaporation rate of the wire source with its lower power dissipation caused a similar shift.

II.6.2 Calibration of the Quartz Crystal Monitor

II.6.2.1 Two Beam Interference Microscopy

The response of the monitor was calibrated against the film deposited on a glass slide positioned adjacent to the quartz crystal. A tungsten wire copper source was used to lay a film on a portion of cleaned glass slide which was masked so that all but $3/8$ of the slide was covered with the copper. For a second evaporation the mask was moved to cover the

FIGURE II.10 Frequency Shift with Temperature
(9.43 MHz Crystal)



3/8 of the slide at the opposite end. The resultant film on the slide was of three thicknesses - due to evaporation (1), due to (1) + (2), and due to (2), with each section separated by a sharp step. The step height was determined by photographing the two beam interference fringes produced in a Baker interference microscope with monochromatic light and measuring the fringe shift by projecting the film negative onto paper where 10 fringes were marked on either side of the step and the shift determined for each. At least two interference patterns were obtained for each step and the mean of the fringe shift was obtained. Ambiguity over the integer number of fringes shifted was resolved by setting up white light fringes which could be identified on both sides of the step. For monochromatic light the fringe shift was related to the step height, t , by:-

$$t = n\lambda/2$$

where n is the total fringe shift

λ is the wavelength of the illuminating light
(in this case 5461 Å).

The step height for each evaporation was related to the thickness of metal deposited on the quartz crystal assuming an inverse square law to allow for the slight difference in source to glass slide and source to quartz crystal distance.

The calibration graph for the 10.915 MHz crystal in the U.H.V. holder is shown in Figure II.11. The sensitivity was 14.3 Hz/Å for copper evaporated onto the electrode of the crystal through the 3/16" collimating hole.

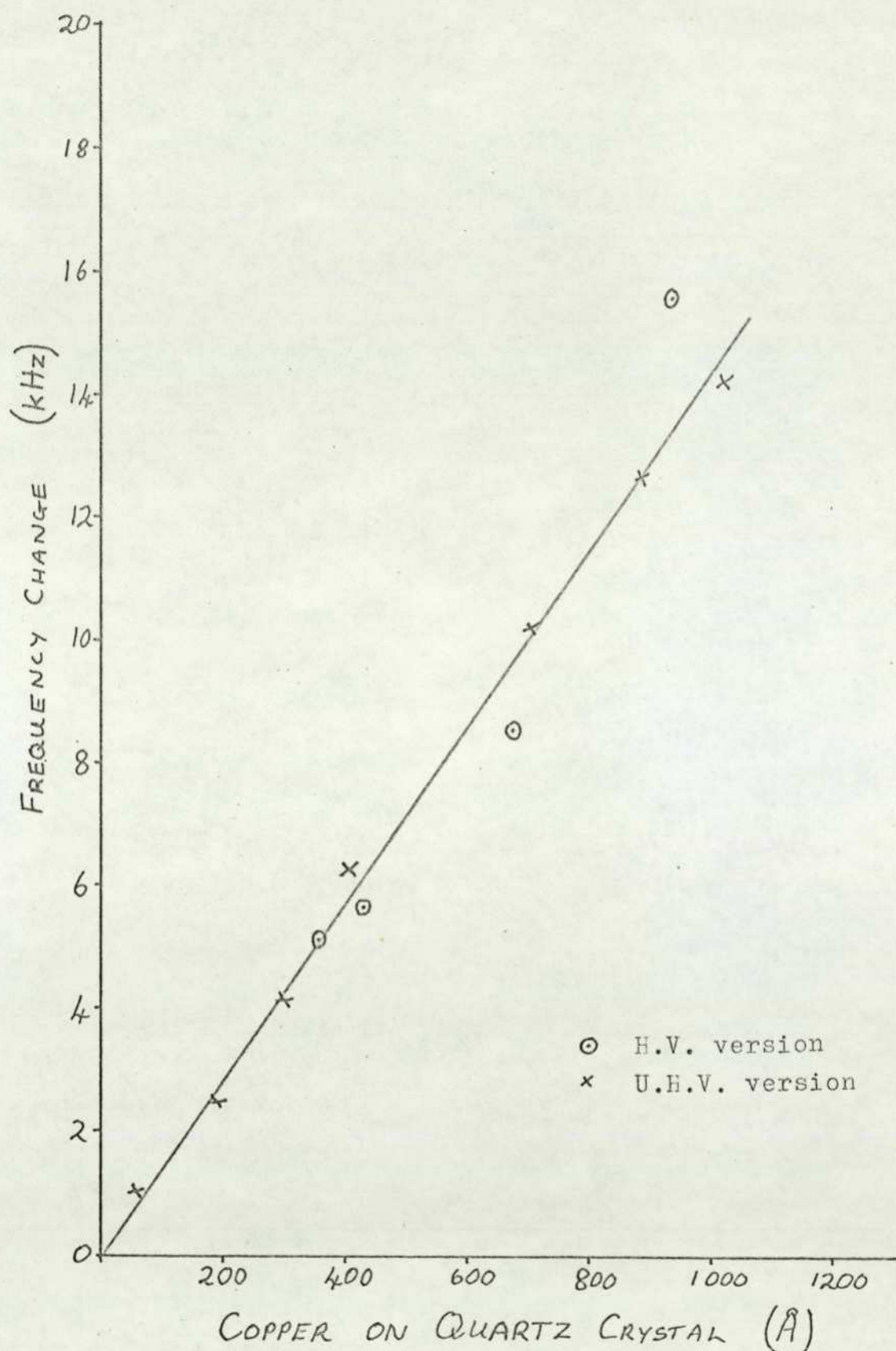


FIGURE II.11 Quartz Monitor Calibration.

The assumptions made in this calibration were that the sticking probability for the copper on the glass was the same as that on the quartz crystal, and that the effective source size was very small compared to its distance from the substrates so enabling the inverse square law of distance to be used without significant error. The error due to the calibrating slide being positioned off the line from the tip of the source to the quartz crystal has two parts. The distance to the slide at 10 mm off axis differed from the perpendicular distance and raised the true thickness of metal on the quartz monitor by 2.5%. The angle χ of the substrate to the beam introduced a further drop of sensitivity of $\sin \chi$ - up to 1.5%. This total error of 4% is comparable to that introduced by position measurement errors of ± 0.5 mm, and the step height of film measured by interference methods. However, the source was found to evaporate from an area much greater than the drop of metal and so led to very large errors due to different effective collimation of the source for the quartz crystal and the platinum substrate. The graph demonstrates the linear response of the monitor in its normal range of operation with total frequency shifts up to 25 kHz.

II.6.2.2 Cross Calibration of Backwards Flux to Forward Flux

When changing the monitoring method from backward flux to forward flux measurements to enable a can source to be used an approximate value of the forward flux crystal response to film thickness was obtained. A close shielded wire source

was operated so as to evaporate onto both crystals giving a thickness on each determined by $1/(\text{distance})^2$. The two crystals were alternately switched to control the oscillator. The cross calibration was used to obtain the response of the forward monitor with the expression:-

$$R_F = R_B \left(\frac{df_F}{df_B} \right) \left(\frac{D_F}{D_B} \right)^2$$

where subscripts F and B refer to forward and backward monitors

R is the response of the crystal in Hz/Å

df is the frequency shift for a certain evaporation.

D is the distance from source to crystal.

The forward response R_F was found to be 15.8 Hz/Å for a crystal of nominal frequency 11.7566 MHz with evaporation through a $\frac{1}{4}$ " aperture. The additional error in this cross calibration, due to measurement accuracy was 11%.

The evaporation characteristics of the wire source, described in section II.5.1, resulted in an over-estimate of deposited film thickness from the above calibrations. A correction factor of 0.36 was determined from subsequent Atomic Absorption measurements and applied retrospectively to hairpin source evaporations.

II.6.2.3 Calibration of Forward Monitor for Evaporation from a Can Source

The errors associated with the previous calibration methods were considerable but were largely eliminated by the following, more direct method. The complete source/monitor cross-

piece assembly was transferred to an auxiliary pumping system where a target was set in the same relative position as the platinum crystal in the LEED system. The target was made up of a 24 mm square glass cover slide with a platinum foil sheet partially covering the glass.

The glass was degreased with acetone while the platinum foil was etched in boiling 50% aqua regia. Both were then left in cold 40% spectroscopically pure nitric acid for 30 mins in a glass dish in which other samples of the same acid had been left to stand to extract soluble materials. The glass and foil were then washed in distilled water, dried on tissues and installed in the vacuum system. After evaporation of a copper film of ~ 5 M-L (estimated from the cross calibration of the forward crystal) the glass and foil were etched separately for 1 hour in 1 ml volumes of the nitric acid, measured using a grade A pipette, and the copper concentration determined by Atomic Absorption. The new figures differed from the cross calibration by a factor of 2 for the platinum foil and more for the glass but when the foil was moved to one edge of the glass a similar average thickness was recorded for both, indicating that the deposition source and collimating system was not producing a uniform flux over more than a small area.

A second series of calibration results was obtained; a foil plate of 10 mm square was held on the centre line of the source/collimating plate system and the film measured by Atomic Absorption. The mean value of the results from 4 films was obtained and was used as the calibration for

subsequent evaporations. The monitor response was 201.2 Hz/Å of bulk copper at the LEED crystal distance.

This calibration was valid for thin films of copper on the platinum in the LEED system if:-

- a) the sticking probability of copper on relatively dirty copper (exposed to the atmosphere) was equal to that on clean copper
- b) the sticking probability of copper on dirty platinum was equal to that on clean platinum
- c) the mass of the film deposited on the quartz crystal was not significantly enhanced by gettering residual gas in the relatively poor vacuum of $\sim 1 \times 10^{-7}$ torr

If the sticking probabilities described in a) and b) were modified equally relative to the clean surfaces the calibration could be used for the LEED system.

The characteristics of film uniformity from the vapour from the can source passing through a collimating plate have been reproduced in a simulation using light. A uniformly illuminated disc of the same diameter (7/32") as the aperture in the copper source was positioned in line with an aperture of 5/16" as in the LEED system, and the light intensity at the LEED crystal position recorded as exposure of a photographic film. The density of this film was measured in arbitrary units using a photometer to measure transmitted light intensity which, after subtraction from the illuminating source level, was plotted against sampling position. The disc size in the plane of the LEED crystal for which the collimating aperture caused no attenuation was 15 mm diameter,

beyond which the source became effectively smaller until extinction at 48 mm diameter.

The result showed that if the copper flux 'illuminated' the source aperture uniformly the flux passing through the R-F coil (internal diameter 12 mm) was uniform within 5% and could be calibrated using a target of up to 15 mm diameter centred on the axis of the source.

This direct method of calibration eliminated the errors of different sticking probabilities of copper on platinum and a substrate such as glass. The atomic absorption result depended on the mass of copper and not the surface structure; island growth or voids in the surface would have increased the thickness measured by interference microscopy for a fixed mass of evaporated film.

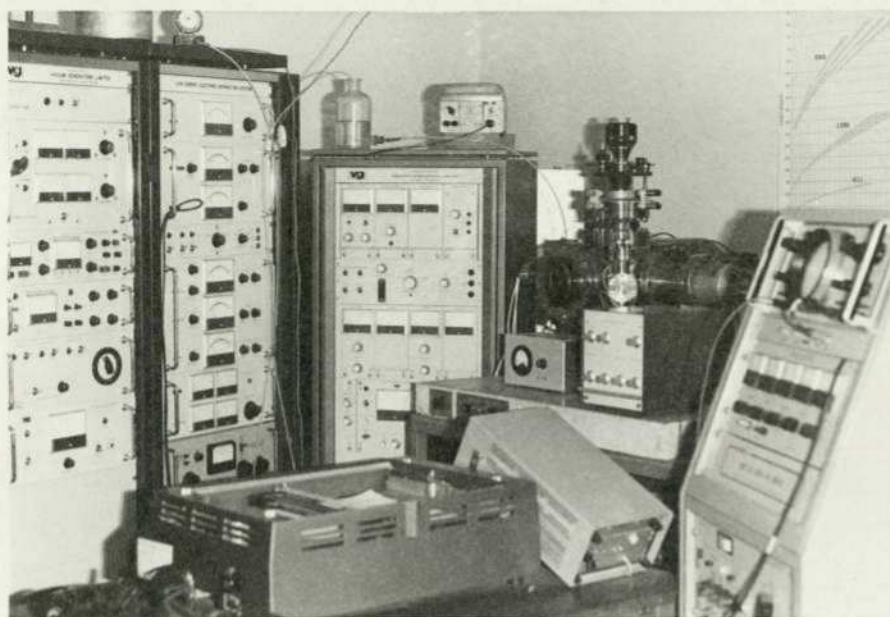
When this calibration of the forward monitor had been used to plot the A.E.S. response to copper the process was reversed to obtain the response of a new crystal (GEC 9.43055 MHz) in the monitor.

II.7 Residual Gas Analysis

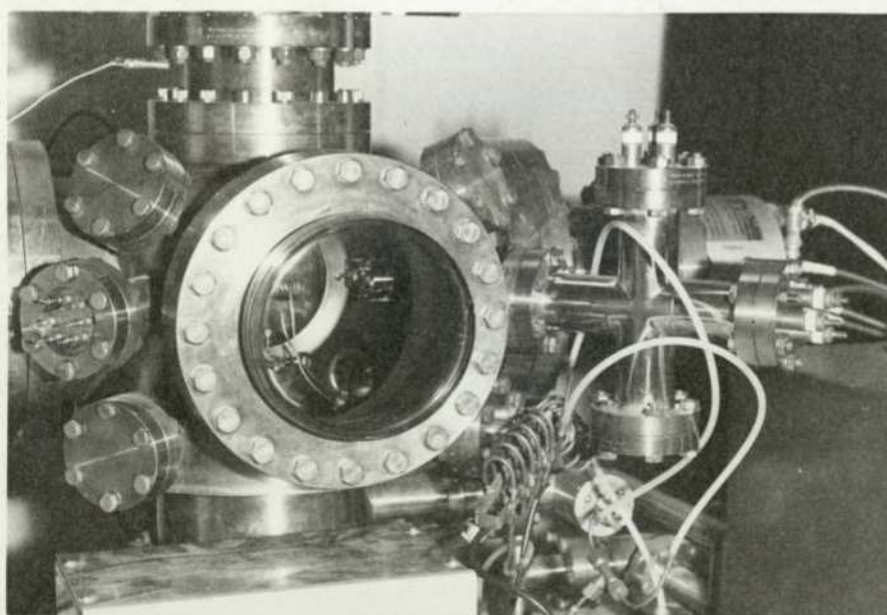
The vacuum system was fitted with an E.A.I. Quadrupole Mass Spectrometer. This type of gas analyser is compatible with a LEED/A.E.S. system as there are no fixed magnets, and the analyser head may be pumped and baked in U.H.V. The unit was mounted in the vacuum system so that the tungsten filament and electron path caused ionisation of the residual gas near the LEED/A.E.S. sample position. The gas ions were accelerated down the axis of the quadrupole analyser. Power supplies in the control unit generated d.c. and radio-frequency modulated d.c. voltages which were fed to the quadrupoles. The analyser rods operated by setting up a complex electrostatic field in which ions having only a small range of mass to charge ratio remained stable near the axis. These ions that were not thrown away from the axis of the rods were detected and amplified in an electron multiplier.

The mass spectrometer was normally used to monitor the gas composition in the mass/charge (m/e) range 0-50 atomic mass units (a.m.u.). After installation of new components it could be used to check for leaks using a helium gas probe. The use of the Analyser was essential for determining the partial pressures of active gases such as oxygen or hydrogen sulphide; the addition of either initially caused desorption of carbon monoxide from the system walls.

The mass spectrum could be displayed on an oscilloscope, normally at a rate of 2 scans/sec or be switched through a Keithley Pico-ammeter for amplification before display



The LEED / A.E.S. Vacuum System and associated control units.



The Vacuum Chamber

FIGURE II.12 The apparatus used in this work.

on a Bryans X-Y recorder. Serious noise was present in the latter display and this problem was not solved. The sizes of the major peaks were noted from the calibrated oscilloscope screen when required. The general method of use has been described by Owens⁽²⁵⁾.

CHAPTER III EXPERIMENTS AND RESULTS

III.1 Introduction

The experimental work was carried out in a system which was being improved continually. The problems encountered in earlier work on the platinum foils and (110) crystals encouraged improved techniques in the studies of the Pt(100) and Pt(111) crystals.

Platinum foil was used for initial work to develop the methods of film evaporation and detection without the use of many expensive single crystals. If the aims described for the foils had been achieved the use of discrete single crystals would have been unnecessary.

In this report LEED patterns are shown in groups of photographs. In each photograph the mask used during printing coincided approximately with the useful area of phosphor of the LEED screen. The system was operated in the Field Free mode and the electron beam energy is given for each result.

The A.E.S. spectra shown are in the most common form of the first differential of the electron distribution i.e. $dN(E)/dE$ plotted against electron energy (E). The modulation voltage from the dial reading is given for each part of the spectrum. The electron energy scale is not marked as it was non linear; peak energies are marked where appropriate. The scan rates were chosen empirically to be at the maximum rates at which no observable loss of resolution occurred at the amplifier band width giving sufficient signal to noise ratio.

III.2 Surface Study of Platinum Foil

Initial studies of platinum foil (99.99% purity, 0.005 inch thickness, supplied by Johnson Matthey Ltd.) were carried out with the following aims:-

- a) to heat treat the foil to develop large crystallites at the surface.
- b) to obtain LEED patterns from large crystallites and take corresponding A.E.S. spectra.
- c) to develop a satisfactory method of evaporating copper.
- d) to obtain the A.E.S. spectrum of a clean platinum surface and a series of spectra of the foil covered by increasing thicknesses of copper.

The development of a variety of crystal faces at the surface should enable the growth meshes of the same copper deposition on different faces to be observed.

III.2.1 The Clean Surface - Pt(Foil)

III.2.1.1 Experimental Procedure - Pt(Foil)

At first, the sample foil was cut to a disc 10 mm in diameter and clamped to a fired pyropholite holder with platinum wires. To enable temperature measurements to be made a Pt/Pt-13%Rh thermocouple was sandwiched between two platinum foil discs in the holder which was machined to support a tungsten spiral coil heater. The outer (sample) disc was untreated before installation in the vacuum system and showed no crystalline features under an optical microscope; slight parallel rolling marks were visible.

The sample foil was radiantly heated from behind by dissipating up to 30 W in the spiral coil filament giving a sample temperature of up to 1000°C . Attempts to obtain higher sample temperatures by this method resulted in excessive feed wire temperatures and possible evaporated contamination. Higher temperatures also caused high degassing rates from the pyropholite which was found subsequently to need a higher firing than the conditions of 950°C for 16 hours used (i.e. 1100°C for 24 hours) to cause better vitrification.

A simple modification to the radiant heating system allowed electron bombardment to be carried out with a power dissipation at the sample limited largely by the power supplies used. The samples were heated to 1300°C by this method but prolonged annealing, more than several minutes, at this temperature caused instabilities in the electron emission current, probably due to ionisation in higher pressure pulses of gas in the sample holder. Operating conditions to give a sample temperature of 1200°C were: filament current 5.2 A, emission current 7 mA, accelerating voltage 600 V.

The temperature of the foil varied considerably across the disc during electron bombardment heating; observation with an optical pyrometer indicated a sample temperature of $\sim 1250^{\circ}\text{C}$ at the centre when the edge indicated $\sim 1050^{\circ}\text{C}$. This uneven heating caused the foil to bow in the holder after extended heating. The principle components of the residual vacuum during heating as determined using the mass

spectrometer were normal hydrogen and carbon monoxide levels but with a high proportion of chlorine.

LEED and A.E.S. results were obtained from the same area of the sample surface by positioning the incident beams using a coordinate system. The sample manipulator enabled calibrated movements of the sample in the incident beam to be made. The vertical lift control directly provided a calibrated shift on the sample while movement horizontally was made using one of the two horizontal traverse screws. The position at which the centre of the sample intercepted the electron beam was determined by scanning across the sample until the diffraction patterns resulting from the LEED gun or channeling patterns from the A.E.S. gun were lost at the edges. The presence of secondary electron current to the crystal could not be used to determine the sample edge position as the low angle of the beam from the glancing incidence A.E.S. gun allowed the beam to strike the sample edge.

III.2.1.2 Results - Pt(Foil)

No LEED patterns were observed after annealing the foil to the limit of the radiant heating system.

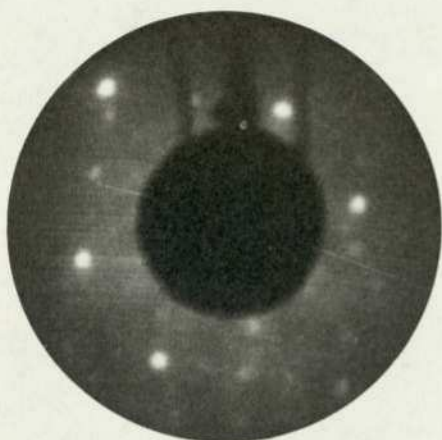
After higher temperature annealing using electron bombardment to obtain sample temperatures of 1100°C - 1250°C polycrystalline areas were detected on the crystal. Many diffraction spots were observed with no obvious symmetry. The zero order beams were detected by their lack of movement when the incident beam energy was varied and these indicated the presence of many crystallites with facets inclined to

the surface of the foil. It should be possible to determine the number and relative angles of the facets in the incident beam by taking a time exposure photograph of the diffraction pattern whilst varying the beam energy. The photograph should then only record as clear spots the stationary zero order beams. However the planned work required crystallites of a similar size to the incident electron beam to allow unambiguous indexing of diffraction features.

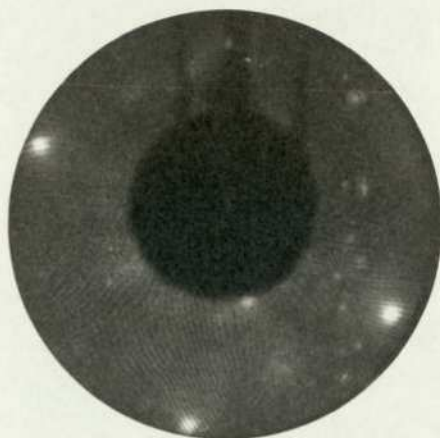
After using in-situ cleaning methods of long annealing at $>1000^{\circ}\text{C}$ in oxygen at $\sim 10^{-7}$ torr and low current argon ion bombardment, areas could be found on the foil sample where only one surface mesh orientation contributed to the observed diffraction pattern. Single mesh patterns are shown in Figure III.1. Of these only diffraction pattern Figure III.1c showed no interference from adjoining crystallites and may be interpreted as 2 domains of $\text{Pt}(111) (2\sqrt{7} \times 2\sqrt{7})R\text{Tan}^{-1}\sqrt{3}/5$. This surface mesh is shown in Figure III.2. The positions of large crystallites were referenced on the foil using the LEED gun and attempts made to take A.E.S. spectra of the surface of the different crystallites.

A referencing system was found impracticable for the following reasons.

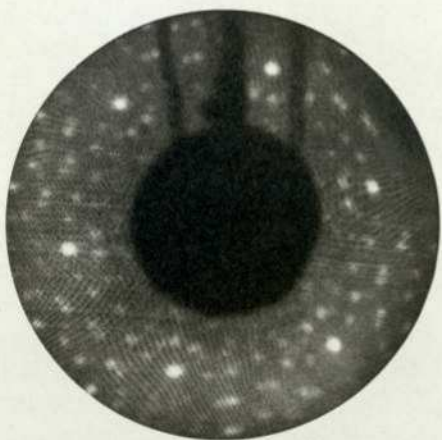
- a) The large and non-cylindrical nature of the LEED gun beam caused a diffuse cut off at the sample edges. Subsequent position measurement was subject to an error of ~ 1 mm.
- b) Although the A.E.S. gun beam focussed more sharply



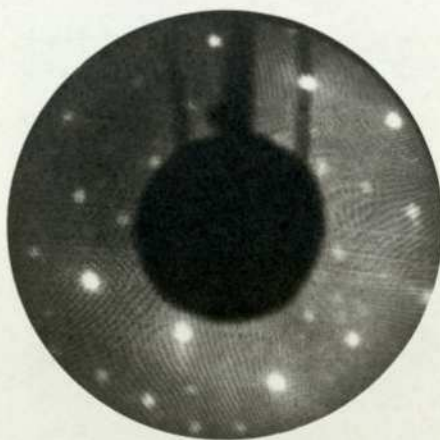
a) 113 V



b) 150 V

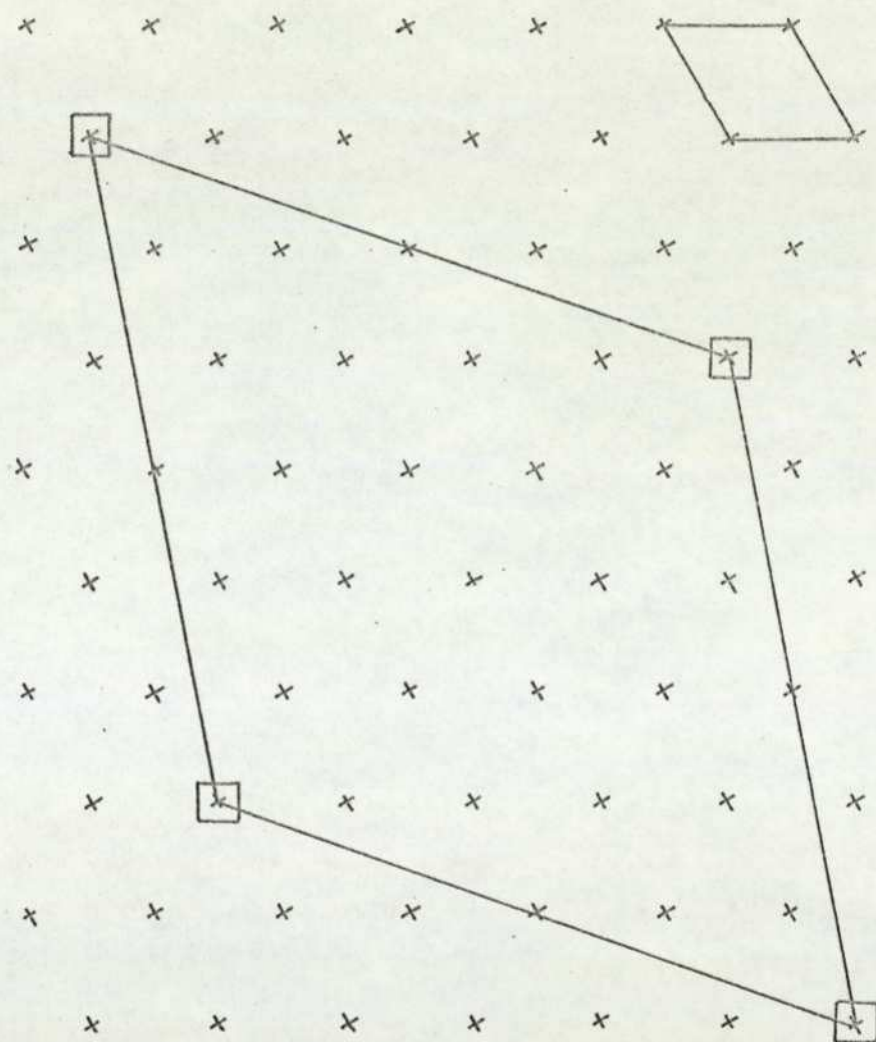


c) 94 V



d) 89 V

FIGURE III.1 LEED patterns from polycrystalline surfaces of platinum foil.



x Base Mesh Atom Position

□ Limit of Surface Mesh

FIGURE III.2 Surface Mesh Pt(111) ($2\sqrt{7} \times 2\sqrt{7}$) on Base Mesh Pt(111) (1×1) Crystallite.

(estimated as 0.5 mm, from the size of the light spot on a fluorescing sample) the low angle of incidence (12°) spread this spot to 2.4 mm in the horizontal direction.

- c) Slackness in the crystal manipulator internal bearing allowed uncontrolled movements of up to 3 mm at the sample position.

Few crystallites were found of sufficient size to give single diffraction patterns.

The sample giving rise to diffraction pattern Figure III.1c was removed from the system and etched in boiling 50% Aqua Regia for 5 mins when microscope examination showed crystallites with minimum surface dimension of up to 1.2 mm.

The A.E.S. spectra obtained from the platinum foils frequently contained several apparently random peaks (which were subsequently explained by electrical interference from the ionization gauge and magnetic interference from the counter-weight of a nearby lift). However, impurities on the platinum surface were clearly seen.

Carbon (273 eV) was the major surface component of all newly installed samples. Although reduced by argon ion bombardment or annealing in oxygen the carbon was never reduced below the detection limit of the instrument. The continuing presence of carbon at the surface was attributed to:

- a) ineffective cleaning by the low current ion gun which degassed heavily (10^{-5} torr 1 sec^{-1} - mainly carbon monoxide).

b) cracking of carbon monoxide on the surface under the influence of the incident A.E.S. gun beam (Lambert and Comrie⁽⁶⁶⁾).

c) diffusion to the surface of bulk carbon during local heating by the focussed electron beam.

Phosphorus was not detected on the acid etched foils after gentle cleaning treatment. However, after prolonged annealing treatment of 2 hours at 800°C a small peak at ~120 eV was seen. This peak became large after a further 5 hours at 800°C.

A peak at 295 eV attributable to calcium was also observed during cleaning and initial copper evaporation operations. The smaller calcium peak at 320 eV could not be resolved from noise to confirm that rhodium from the foil or thermocouple was not present.

Sodium (~1000 eV) was present at the surface but the signal was subject to considerable noise.

Potassium was also suspected at the surface but coincided with a platinum peak at the low resolution available.

Antimony (460 eV) was found as a significant peak during the surface treatments.

Serious contamination of the foil samples was attributed to the use of the pyropholite holder. The high degassing rate in the filament space would be responsible for a high sputtering rate for filament and surrounding ceramic materials. Such a holder was not suitable for the preparation and maintenance of clean surfaces.

III.2.2 Copper Evaporation on to Platinum Foil

III.2.2.1 Experimental Procedure

A tungsten hairpin source was used and positioned sufficiently far from the sample to allow close control of the evaporation rate. Operation of the source, after initial outgassing and evaporation onto a valve acting as a shutter, raised the system pressure during evaporation to $\sim 1 \times 10^{-9}$ torr from the base pressure of 2×10^{-10} torr. The characteristics of the source are described in section II.5.1. The copper vapour leaving the source was collimated through two circular apertures, the first to protect the isolating valve from excessive metal build-up which could have interfered with its operation, and the second to restrict copper evaporation in the large vacuum chamber to the sample area. The pyropholite sample holder was fitted with a stainless steel sheet collar to prevent copper deposition on the LEED screen and grids. This form of shield restricted viewing of diffraction patterns to outer areas only.

III.2.2.2 Results

As the LEED patterns at the surface before evaporation could not be accurately referenced no attempt was made to follow the effect of evaporating metal.

Due to the unexpected characteristics of the hairpin source less copper was evaporated than anticipated. An average surface coverage of ~ 0.1 monolayers was seen with the A.E.S. as a peak at 108 eV. The anticipated higher energy signal peaks from copper were indistinguishable from the large noise level at analyser energies of 600-1000 eV at

lower coverages.

An A.E.S. spectrum taken of a foil surface with 0.1 M-L of evaporated copper is shown in Figure III.3. The many impurities present may be seen.

As the noise present in the high energy range (600-1000 eV) was particularly severe on polycrystalline samples due to magnetic deviation of the incident beam an attempt to obtain a film thickness/Auger signal calibration was not attempted further.

III.2.3 Foils - Summary

- 1) Crystallites of sufficient size for LEED and A.E.S. study could be grown in platinum foil by annealing at $>1000^{\circ}\text{C}$ for several hours.
- 2) Although a referencing system was devised to locate specific areas of the sample for both LEED and A.E.S. studies the slackness of the manipulator was too large to allow the system to be used.
- 3) Surface contamination by carbon, sulphur, phosphorus, calcium and antimony was observed. Much of this may have originated from the pyropholite sample holder.
- 4) The sensitivity of the A.E.S. to evaporated copper was low. The rough polycrystalline surface contributed a high noise level as the electron beam was affected by small magnetic or electrostatic fields. The rough surface may have caused shadowing of surface copper in 'valleys'.

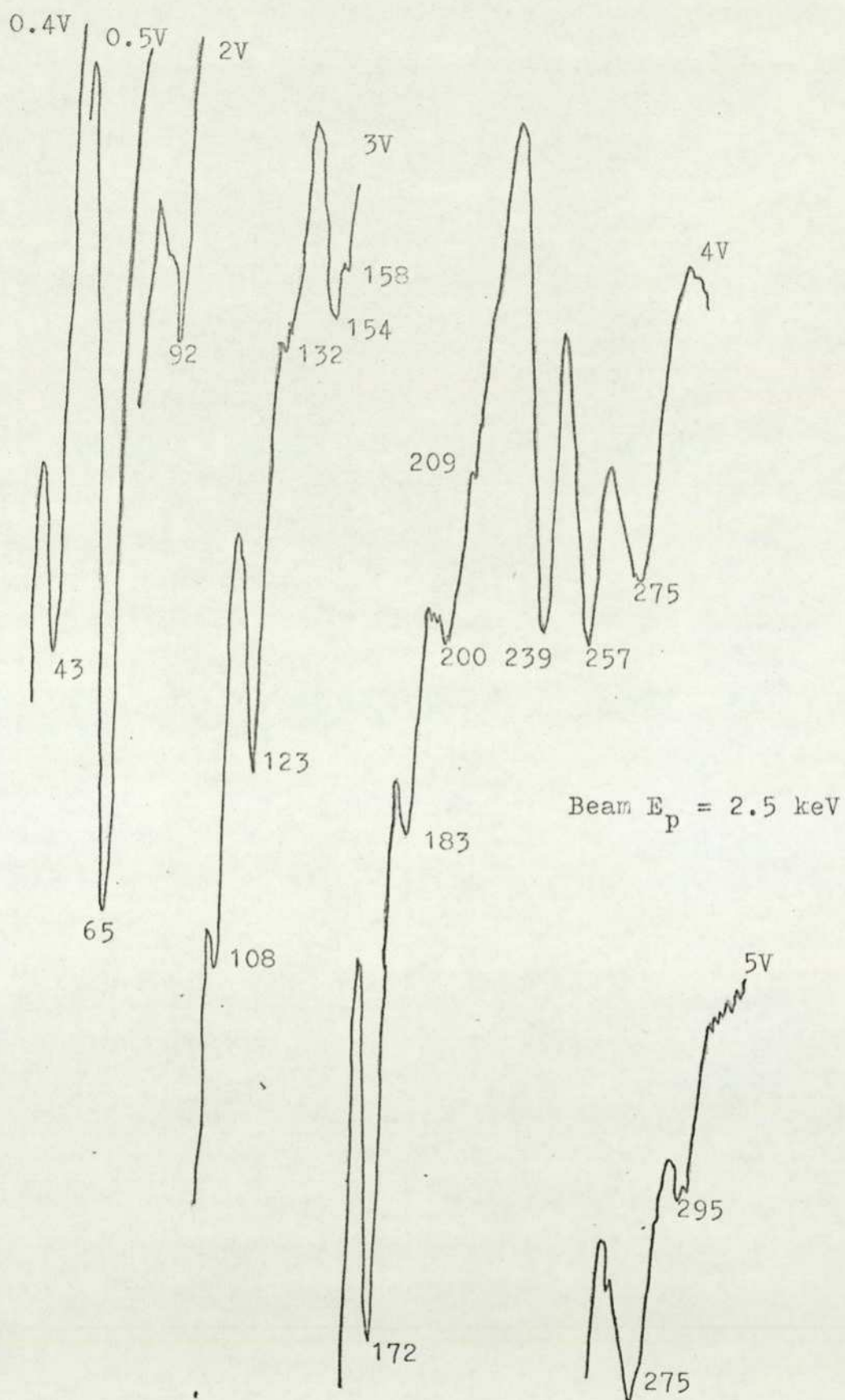


FIGURE III.3 Auger spectrum from platinum foil. Low coverage of copper, impurities present.

III.3 Surface Study of Pt(110)

III.3.1 The Clean Surface

III.3.1.1 Experimental Procedure

An irregular single crystal, supplied by Metals Research Ltd., with its face spark cut and spark planed to within $\frac{1}{2}^{\circ}$ of the (110) plane was cut to give a sample 2.0 x 2.5 mm of thickness 1.0 mm. These cuts were made with an 80-100 mesh diamond grit cutting blade rotating with an edge speed of 20 m. sec⁻¹ while the crystal was mounted on a softwood block with Araldite.

The crystal was then set in a mounting plastic and polished first on wet fine emery cloth (600 grade) until uniformly marked. It was then washed in an ultrasonic bath to prevent carry-over of coarse grit, and polished on a 12 inch 1 μ m diamond abrasive cloth on a wheel rotating at 250 r.p.m. The direction of cut was perpendicular to that of the emery polishing, and was continued until the emery marks disappeared. After dissolving the crystal from the plastic in acetone followed by a 2 min. etch in boiling 50% aqua regia it was clipped onto the front of a foil disc holder and a Pt/Pt-13%Rh thermocouple inserted at the side of the crystal. The holder and crystal were then etched for 5 mins., washed in distilled water, and installed in the sample heater unit in the vacuum system.

The temperature recorded by the thermocouple was intermediate between the electron bombarded foil and the outer face of the single crystal. The recorded temperature

was estimated to be $\sim 100^{\circ}\text{C}$ higher than the crystal front face temperature when 1100°C was recorded.

The inability to clean the surface using the equipment available up to this stage led to the development of the inherently cleaner method of high frequency induction heating. The system was modified to use this method before further study of the crystal.

The Pt(110) crystal was heavily etched in boiling 50% aqua regia for 10 mins before insertion into a new platinum foil holder to increase the effective area for R.F. heating. A Pt/Pt-13%Rh thermocouple was spot-welded to the foil near the crystal and two 0.25 mm support wires fitted for attachment to a barrel connector on the crystal manipulator. The crystal assembly was again etched for 3 mins., washed in distilled water and installed in the LEED/A.E.S. system.

The crystal was then cleaned by a series of argon ion bombardment treatments at a higher pressure (1×10^{-4} torr of argon) than used earlier and with a magnet positioned for maximum ion current (7.5 nA mm^{-2}). This was alternated with annealing treatment at up to 600°C in 1×10^{-7} torr of oxygen for periods of 10 mins.

III.3.1.2 Results - Pt(110)

III.3.1.2.1 Electron Bombardment Heating

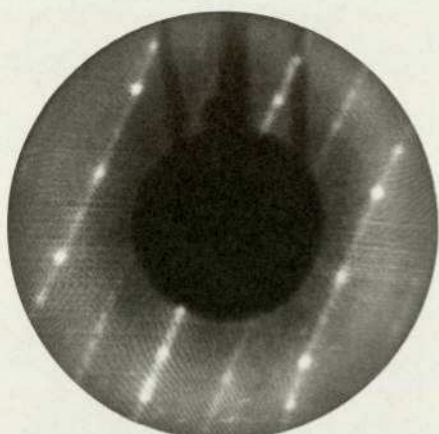
After bakeout and degassing of filaments to obtain a base pressure of 6×10^{-10} torr in the system, A.E.S. scans of both the crystal and the backing foil showed large coverages of carbon and sulphur with small peaks due to phosphorus, calcium and antimony. No LEED patterns were visible at this

stage.

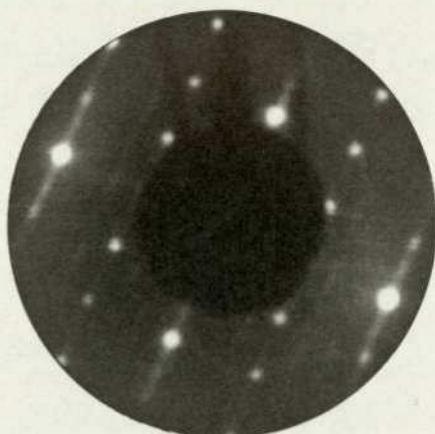
The ~~argon~~ ion gun, operating at a current density of 2 nA mm^{-2} was ineffective for cleaning. A series of annealing treatments in vacuum and oxygen pressure of $\sim 5 \times 10^{-8}$ torr was then carried out until LEED patterns could be observed and surface impurities were reduced. Phosphorus was found at increased concentration at the surface after prolonged annealing in vacuum but was reduced in oxygen. Prolonged annealing in oxygen (650°C for $4\frac{1}{2}$ hours in a pressure of oxygen of 5×10^{-8} torr) resulted in a large oxygen Auger peak at 510 eV. When the crystal on its backing foil was removed to etch off surface contaminants a black deposit was found on the back of the foil. This was resistant to a mixture of strong acids and appeared to be sputtered tungsten.

After reinstalling followed by a 15 min. anneal at a recorded temperature of 1250°C well defined LEED patterns could be seen. Figure III.4a shows a mixed pattern. The strongest features were $\text{Pt}(110)-(1 \times 2)$ but $(1 \times n)$ and $(2 \times n)$ spots with $n=2,3$ and higher were present. These meshes are shown in Figure III.5. This pattern corresponded to an A.E.S. spectrum showing a large calcium peak but low phosphorus, sulphur, carbon and oxygen. Figure III.4b from the crystal showing a similar A.E.S. spectrum indicated the development, after further annealing, of the $\text{Pt}(110)-(2 \times 2)$ with some $\text{Pt}(110)-(3 \times n)$ features.

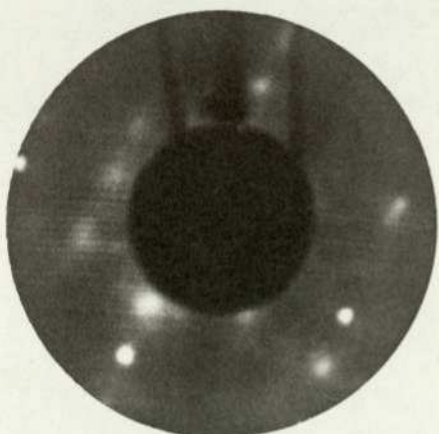
Further high temperature annealing was found to decrease all surface contaminants except calcium. The major peak was recorded at as high as 300 eV when nearby platinum and



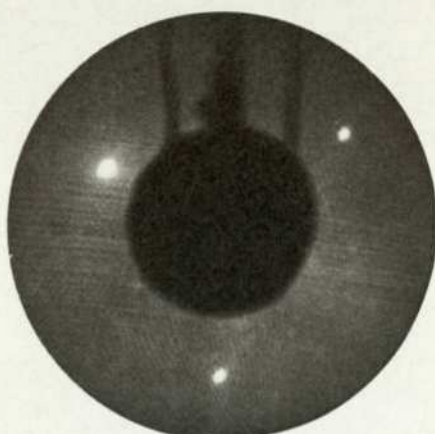
a) 101 V



b) 59 V



c) 54 V



d) 46 V



e) 27 V



f) 135 V

FIGURE III.4 LEED patterns from Pt(110) with surface impurities. a-d) After electron bombardment heating. e,f) R-F heating. d) Surface impurity 0.1 M-L Copper.

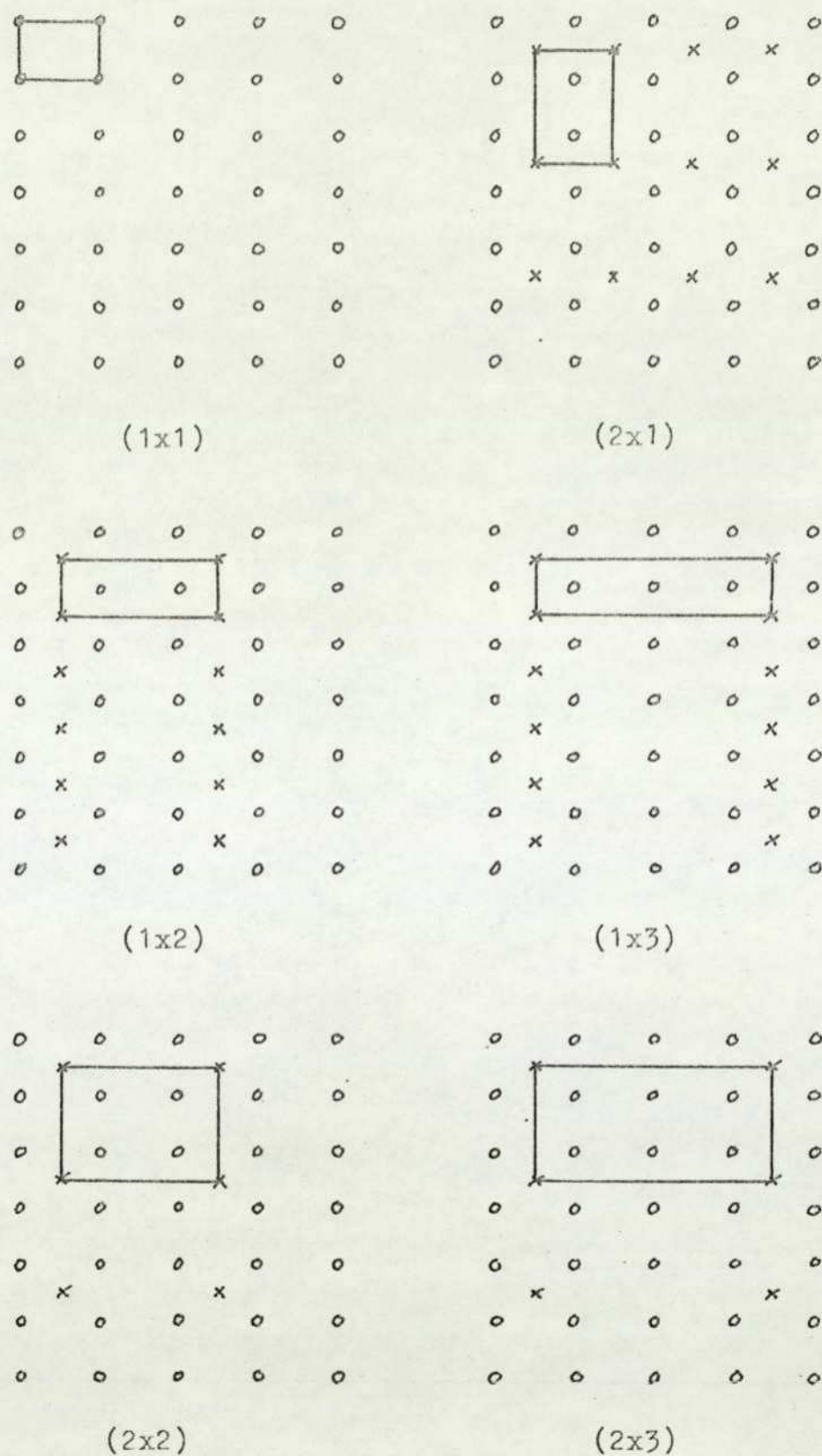


FIGURE III.5 Pt(110) surface meshes.

Domains of these meshes contribute to the LEED patterns shown in Figure III.4

carbon were within + 2 eV of the values of ref. 114. However the presence of a small peak recorded at 324 eV is typical of calcium and not rhodium.

Attempts to clean the surface further using the argon ion gun (ion current $\sim 2 \text{ nA.mm}^{-2}$) resulted in an increased carbon signal and unchanged calcium level.

Figure III.4c shows a LEED pattern from a high calcium level Pt(110) crystal with a Pt(110)-(2x2) diffuse pattern with bright facet features.

III.3.1.2.2 R-F Heating

The improved cleaning procedure resulted in a surface showing, by A.E.S., no significant impurity peaks except small carbon (273 eV) and oxygen (516 eV) peaks. Crystal annealing in oxygen at less than 1×10^{-7} torr was limited in ability to remove carbon due to build up of carbon monoxide in the system as the components of the R-F heating system over-heated. The resultant surface showed both carbon and oxygen peaks by A.E.S. Surface carbon annealed at 800°C for several minutes ordered to a graphite structure with its characteristic ring diffraction where the ordering was low (Figure III.4e). Annealing to higher temperatures up to 1000°C in 5×10^{-8} torr of oxygen reduced the carbon level further and removed the ring diffraction pattern due to the graphite surface mesh. Despite the lower surface impurity level (small oxygen, carbon and sulphur) the surface mesh remained complex (Figure III.4f). The lowest carbon level was observed after prolonged annealing in oxygen ($600 - 900^{\circ}\text{C}$ at 5×10^{-8} torr of oxygen). No other impurities were observed in an

A.E.S. spectrum from 0 - 1100eV except a very large oxygen peak. After the crystal was annealed at 1100°C for 3 mins in vacuum the oxygen peak almost disappeared but large carbon and moderate calcium signals were obtained. The calcium signal varied with the beam position on the crystal.

III.3.2 Copper Evaporation on Pt(110)

The contaminated Pt(110) crystal exhibiting complex LEED patterns was exposed to the copper source operating at a low evaporation rate.

The principal surface impurity before evaporation was calcium recorded at 299 and 323 eV. After evaporation of <0.1 M-L of copper small broad peaks corresponding to copper were observed in the 780 - 940 eV range while the relative heights of the calcium and platinum peaks were unchanged. A large broad peak at ~205 eV appearing after evaporation was well displaced ^{from} chlorine (181 eV); argon (200 and 215 eV) had not been used before the evaporation. The LEED pattern resulting from this low coverage was clear Pt(110)-(1x1) with no other features present (Figure III.4d).

III.3.3 Pt(110) - Summary

- 1) Deposits on the back of the crystal indicated heavy sputtering of tungsten from the filament and pyrophosphate from the holder. The crystal had developed high impurity levels while annealing.
- 2) Impurities (calcium and phosphorus) were easily etched from the surface and were slowly replaced on annealing. High calcium-levels were detected on annealing after high surface oxygen levels had been detected.

3) No clean surface LEED patterns were obtained. Impurities stabilised patterns of the type Pt(110)-(1xn).

4) The Pt(110)-(1x1) LEED pattern was observed after a submonolayer deposition of copper. This may be compared to the stabilising effect of copper on Pt(100).

III.4 Surface Study of Pt(111)

III.4.1 The Clean Surface

III.4.1.1 Crystal I

III.4.1.1.1 Experimental Procedure

This crystal was supplied by Metals Research Ltd. from a 5N (99.999%) purity boule and oriented to within $\frac{1}{2}^{\circ}$ of the (111) face, cut and planed by spark erosion. It was mounted, and polished on abrasives in the following order; 600 grit emery paper, 6 μm diamond paste then 1 μm diamond paste on polishing cloths. After etching in boiling 50% aqua regia for 3 mins. the crystal was spot welded at an edge to a 0.25 mm 4N purity platinum support wire. After a further 2 mins etching the crystal was installed in the LEED/A.E.S. system. After bakeout and degassing the system to give a pressure of 2×10^{-10} torr the crystal was annealed in oxygen at a pressure of 6×10^{-8} torr at 920°C .

III.4.1.1.2 Results

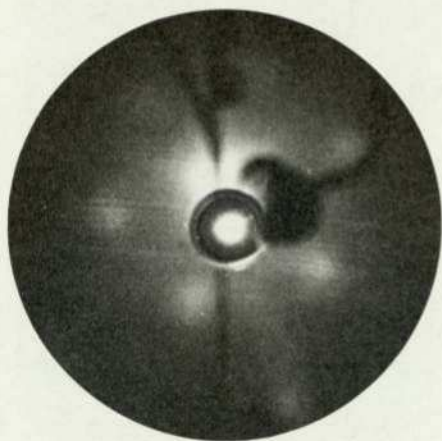
The reduction in system contamination relative to earlier work was shown by the high ratio (17 : 1) of the $m/e = 32$ oxygen peak to the carbon monoxide 28 peak seen on the mass spectrometer. After further annealing at $600 - 750^{\circ}\text{C}$ for

several hours the LEED pattern observed was a diffuse Pt(111)-(1x1) and the A.E.S. showed moderate size carbon 274 eV and very small calcium 294 eV peaks as the only surface impurities. A large oxygen peak (516 eV) appeared after annealing for 4 hours at 750°C in 5×10^{-8} torr of oxygen; the LEED pattern corresponding to this was a diffuse Pt(111)-($\sqrt{3} \times \sqrt{3}$)R 30° (Figure III.6a). The A.E.S. spectrum showed the presence of sulphur (Figure III.7).

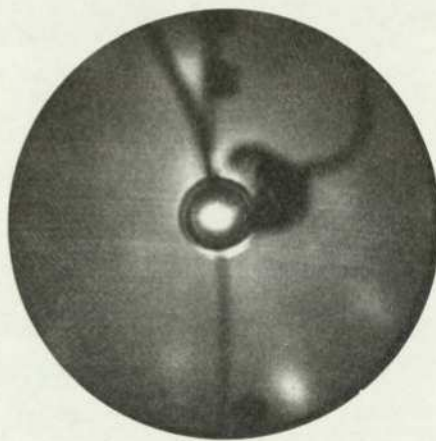
A hydrogen treatment (1×10^{-8} torr at 910°C for 1 hour) was used to reduce the surface oxygen but the carbon level increased and calcium was again detected. The LEED pattern was then a diffuse Pt(111)-(2x2) (Figure III.6.b).

The crystal was removed from the system and etched for 5 mins. in boiling 50% aqua regia before being returned and pumped to an ultimate pressure of 1×10^{-10} torr with major components hydrogen (m/e = 2), water (18), carbon monoxide (28), chlorine (35,36,37) and carbon dioxide (44). An oxygen treatment of 5×10^{-8} torr at 750°C for 15 mins. followed by a 16 hour argon ion bombardment and an anneal up to 950°C produced a surface giving sharp Pt(111)-(1x1) diffraction patterns (Figure III.8c,d). The presence of ordered carbon was seen as a weak ring outside the first order platinum diffraction spots. After further annealing at 950°C in 1×10^{-7} torr of oxygen the carbon level was still very high and a well ordered ring pattern showing a two domain graphite mesh was observed (Figure III.6c,d).

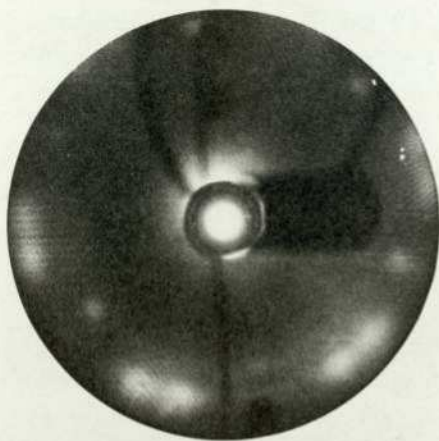
At this stage it was possible to remove most surface carbon by annealing in oxygen (1×10^{-7} torr at 700°C for



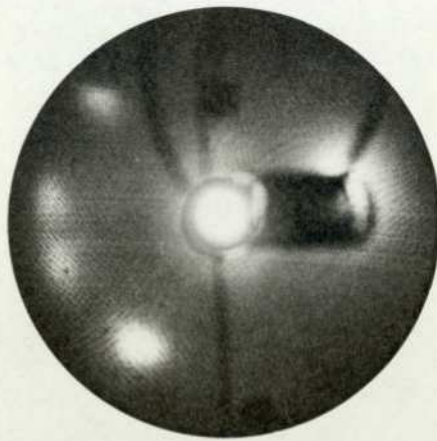
a) 41 V
Pt(111) ($\sqrt{3} \times \sqrt{3}$)R30°



b) 43 V
Pt(111) (2x2)



c) 41 V
Graphite on Pt(111)



d) 30 V

FIGURE III.6 LEED patterns from a Pt(111) surface in the presence of impurities.

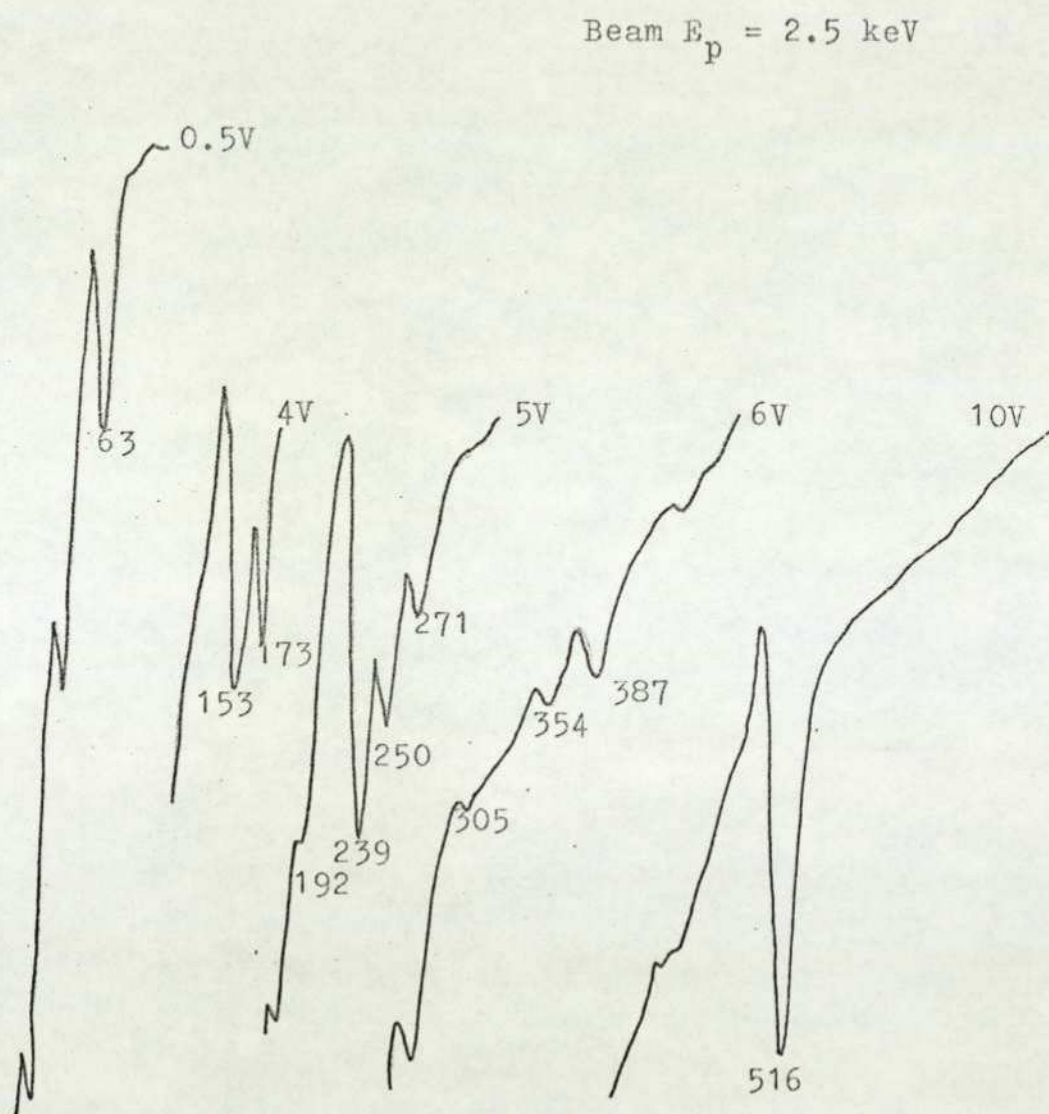
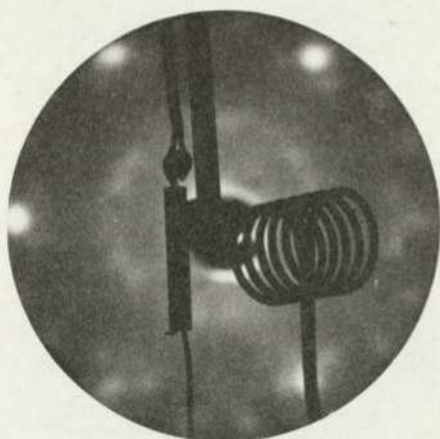
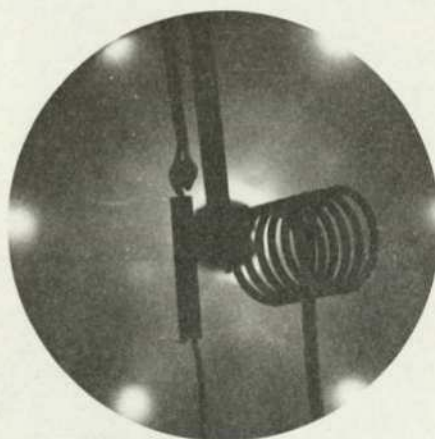


FIGURE III.7 Auger spectrum from Pt(111) crystal after oxygen treatment.

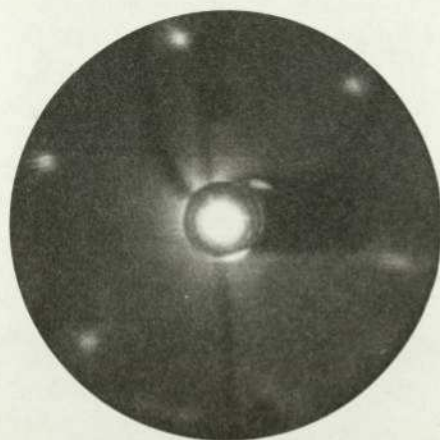


a) 62 V



b) 50 V

Pt(111) + Surface Oxygen



c) 64 V



d) 49 V

Pt(111) + Surface Carbon

FIGURE III.8 LEED patterns from Pt(111) in presence of impurities.

several hours) but this resulted in surface oxygen being detected by A.E.S. Insufficient oxidation of a carbon covered surface resulted in a graphite mesh diffraction pattern while further oxidation could lead to a stable oxide overlayer. This chemical treatment could not be sufficiently controlled to give a clean surface. More efficient argon ion bombardment methods were then developed to overcome this.

After a sequence of argon glow discharge sputtering, annealing the sample in oxygen at 2×10^{-7} torr at 750°C then further glow discharge sputtering, A.E.S. of the Pt(111) crystal showed predominantly oxygen. After annealing at 750°C for 3 hours the oxygen peak was reduced and a small calcium peak observed, with also small sulphur and carbon peaks (Figure III.9). This appearance of calcium when annealing to decrease the surface oxygen level was similar to that observed on the Pt(110) face.

A series of oxygen and hydrogen annealing treatments for a total of 350 L and 130 L respectively at approximately 900°C produced a stronger complex pattern similar to that observed earlier, ~~Figure III.~~ This clearer pattern is shown in Figure III.10a-d. The A.E.S. spectrum obtained from this surface showed a large oxygen peak and small carbon, tin and calcium impurities.

This surface was then argon ion bombarded overnight to a total of 10 μA - hrs and the crystal annealed at 1000°C for 10 mins. The resultant LEED pattern showed a clean Pt(111)-(1x1) and the A.E.S. spectrum contained very low impurity peaks.

(NOTE : 1 L = 1 Langmuir $\equiv 10^{-6}$ torr sec)

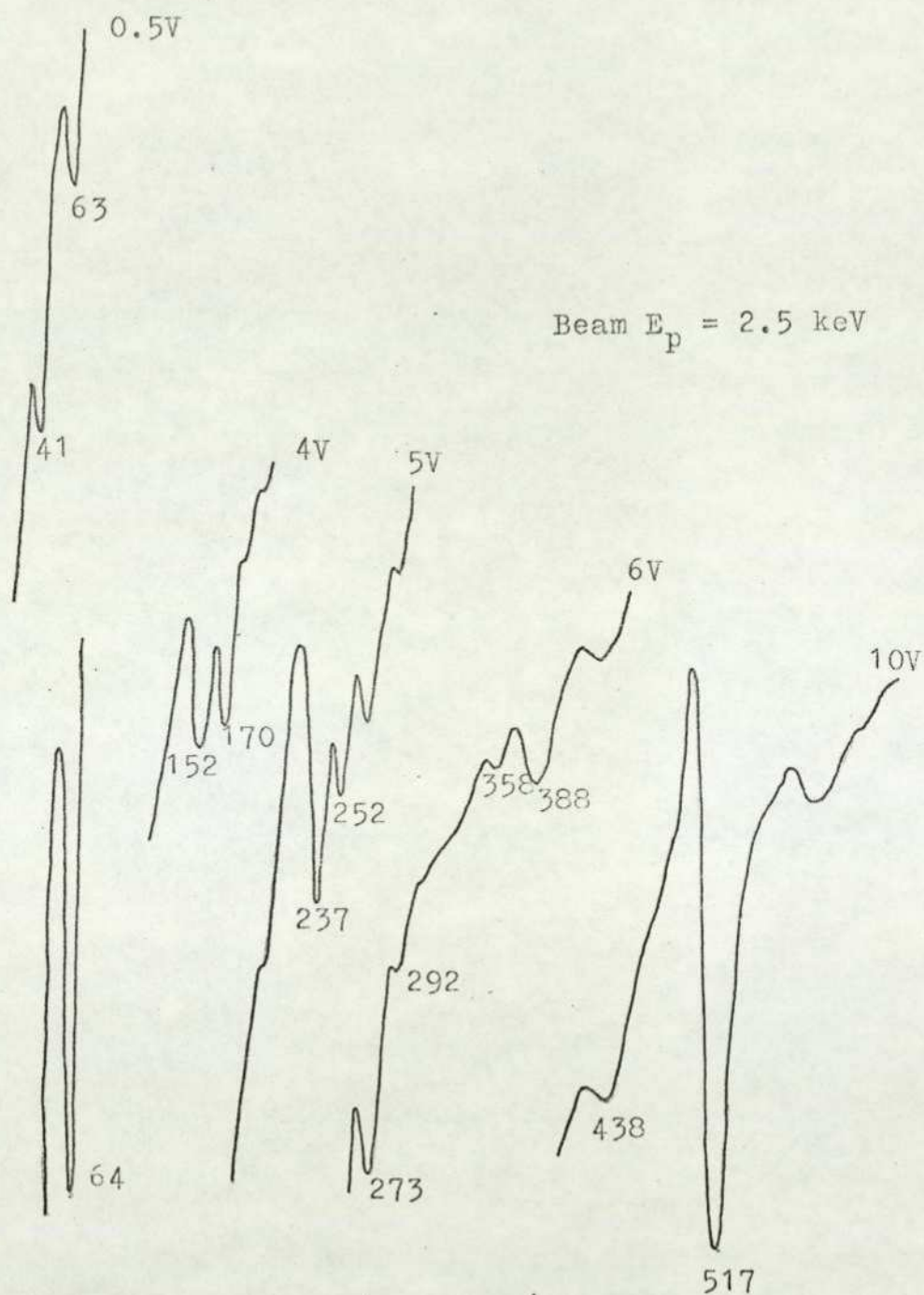
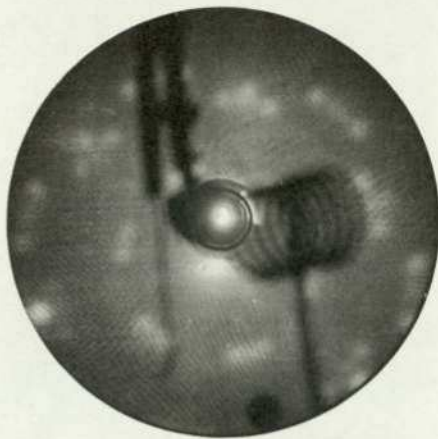


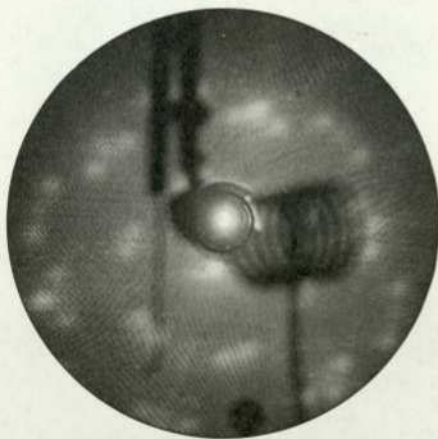
FIGURE III.9 Auger spectrum of a Pt(111) crystal.
 Annealed after oxygen treatment.
 A small calcium peak (292 eV) is present.



a) 36 V



b) 60 V



c) 67 V



d) 39 V

FIGURE III.10 LEED patterns, Oxygen and Carbon on Pt(111).

III.4.1.2 Pt(111) Crystal II

III.4.1.2.1 Experimental Procedure

A larger half elliptical Pt(111) crystal was cut as before and polished with the following sequence of abrasives until a highly reflective surface was obtained.

- 1) 600 grade emery paper
- 2) 8 μ m alumina
- 3) 3 μ m alumina
- 4) 0.3 μ m alumina
- 5) Etched in boiling 50% aqua regia for 3 mins.

The crystal was then spot welded to 0.25 mm 4 N purity platinum support wires and the cleaning steps 4 and 5 were carried out two more times.

In the vacuum system the crystal was annealed at 1050°C, argon ion bombarded at $\sim 0.75 \mu$ A for 60 hours and annealed at 1100°C for 4 hours. During this heating treatment sodium (23) potassium (39) and calcium (40) ions emitted from the hot crystal were detected in the mass spectrometer with the ioniser off. No emission was observed from the hot R.F. coil with no sample heating in it. The emission was most easily detected when the sample was biased at +220 V above earth.

III.4.1.2.2 Results

Surface carbon present after this anneal was largely removed by annealing for 2 hours at 950°C in 3×10^{-7} torr of oxygen followed by argon ion bombardment at 1 μ A for 2 hours and an anneal at 950°C for 10 mins. This resulted in low sulphur and carbon signals and a small tin peak at 439 eV. The LEED pattern was then Pt(111)-(1x1). A further oxygen/hydrogen cleaning sequence brought weak features of a LEED

pattern associated with oxygen (Figure III.8a). A further short argon ion bombardment of $1/10 \mu\text{A}$ for 1 hour only partially removed this pattern and left a weak $\text{Pt}(111)-(\sqrt{3}\times\sqrt{3})\text{R } 30^\circ$ (Figure III.8b).

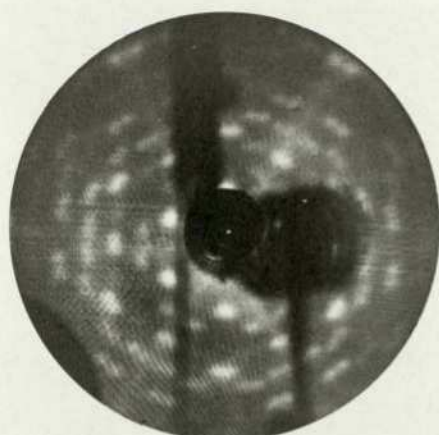
III.4.1.3 Heavy Surface Oxide Growth on Pt(111)

When the crystal was annealed at 1000°C for 5 mins in 1×10^{-6} torr of oxygen the surface gave rise to a complex LEED pattern Figure III.11a-c. The corresponding A.E.S. spectrum is shown in Figure III.12; the carbon level is very low but sulphur has not been entirely removed.

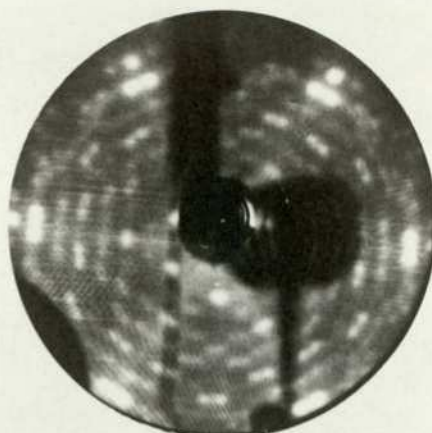
Evaporation of $\sim 0.6 \text{ Cu}(111)$ M-L of copper on this surface caused no noticeable change in pattern, see Figure III.11d,e but was clearly detected by A.E.S.

This surface was then cleaned with the new higher current ion gun at $4 \mu\text{A}$ for 35 mins which removed both copper and oxygen but left small carbon and tin peaks after annealing at 930°C for 20 mins. The LEED pattern was then a $\text{Pt}(111)-(2\times 2)$ as shown in Figure III.11f.

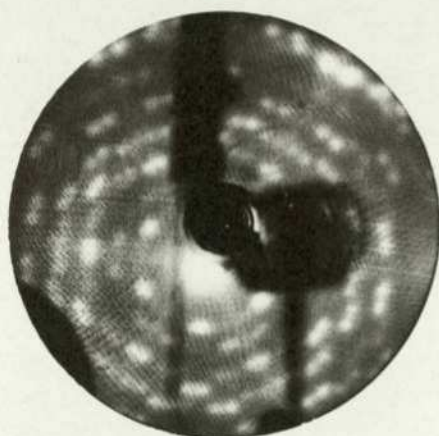
The surface oxide growths were very stable, remaining after annealing in vacuum to over 1000°C . The structure was unaffected by the limited copper deposition unlike the more transient $\text{Pt}(100)-(5\times 1)$ and $\text{Pt}(110)-(1\times n)$ complex patterns. The diffraction spots may be indexed as a $\text{f.c.c.}(111)- (4\sqrt{3}\times 4\sqrt{3})$ in which the basic f.c.c. mesh has a nearest neighbour spacing 10% greater than the platinum spacing of $2.774 \text{ \AA}$. Two domains exist, rotated through $\pm 4^\circ$ from the substrate mesh.



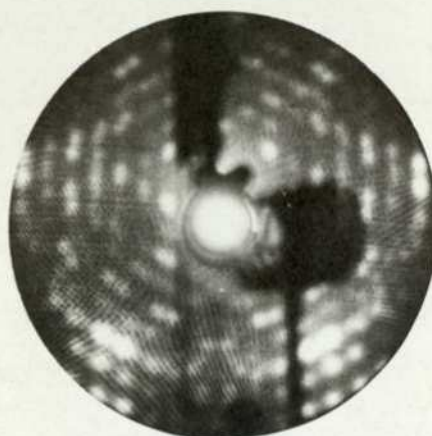
a) 42 V



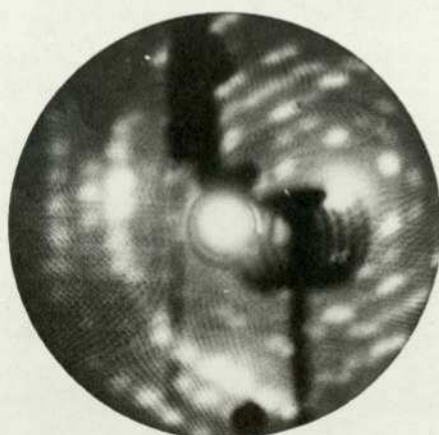
b) 58 V



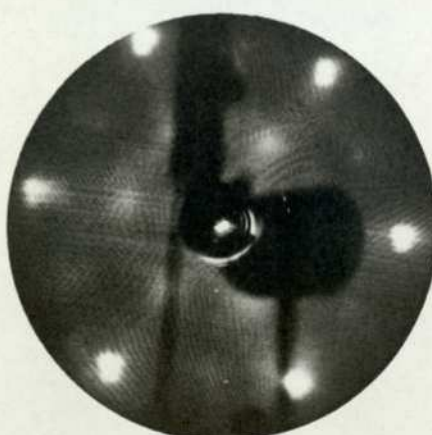
c) 38 V



d) 54 V



e) 47 V



f) 67 V

FIGURE III.11 LEED patterns. Pt(111) after annealing in Oxygen. a-c) Oxygen as major contaminant. d,e) Additional 0.6 M-L of Copper. f) After ion bombardment Surface mesh is f.c.c.(111) ($4\sqrt{3} \times 4\sqrt{3}$) - see text.

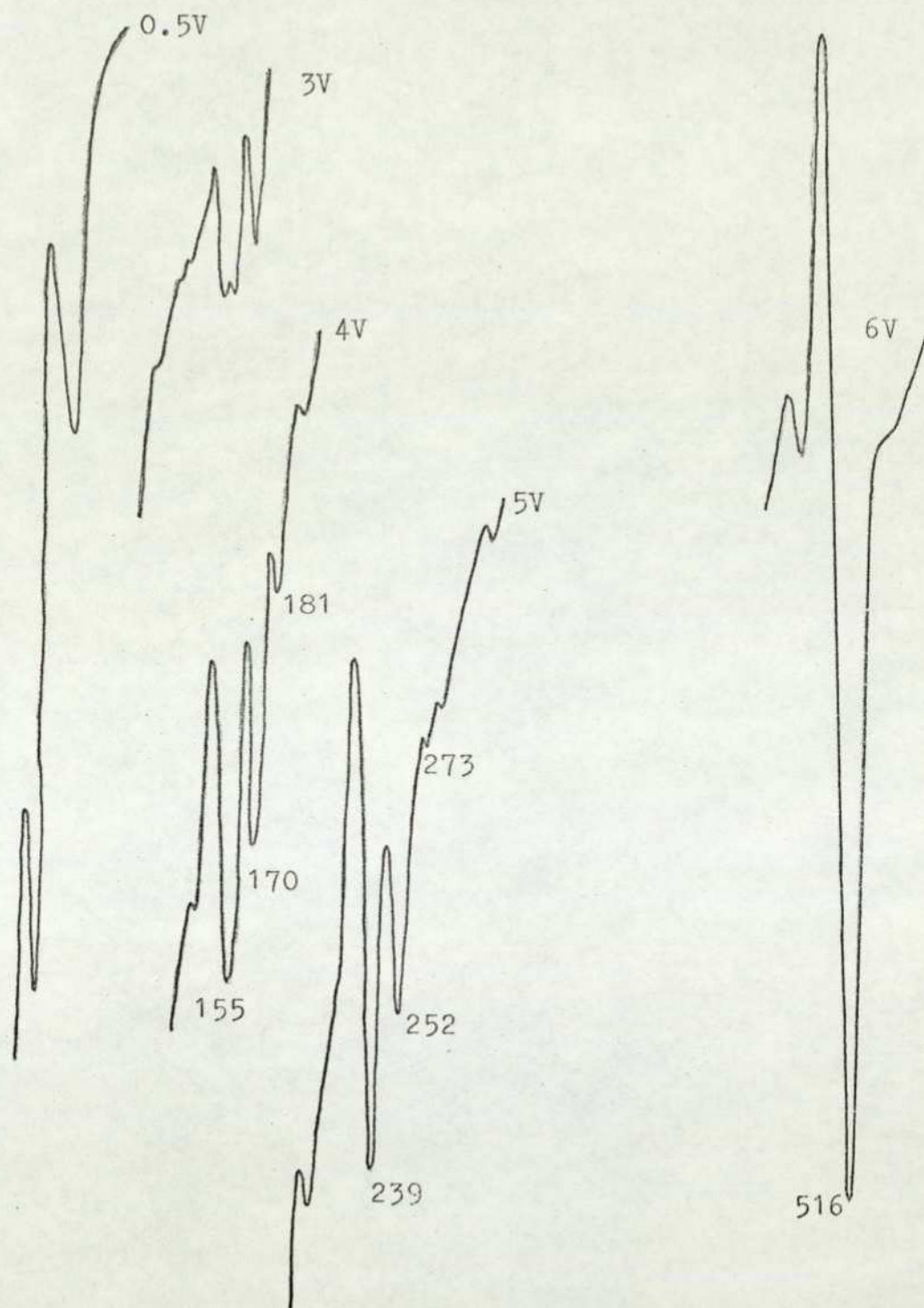


FIGURE III.12 Auger spectrum from Pt(111) after heavy oxygen/annealing treatment.

III.4.1.4 Pt(111) - Summary

- 1) Carbon diffused to the surface of the crystal when annealed $>700^{\circ}\text{C}$. Oxygen removed this surface carbon, but at temperatures below 700°C when the surface carbon replacement rate was low surface oxygen was detected by A.E.S.
- 2) The lowest surface impurity levels were obtained by annealing at $850-1000^{\circ}\text{C}$ in an oxygen pressure of $1-5 \times 10^{-7}$ torr for 10-200 mins. The severity of the treatment was determined by the surface carbon level. The resultant surface oxygen was removed by argon ion bombardment followed by an annealing at $900-1000^{\circ}\text{C}$ for a few minutes.
- 3) The cleanest surface produced, with low sulphur and carbon levels detected by A.E.S., gave a Pt(111)-(1x1) LEED pattern.
- 4) Calcium was detected at the surface after annealing an oxygen covered crystal at $>900^{\circ}\text{C}$.

III.4.2 Copper Evaporation onto Pt(111)

III.4.2.1 Experimental Procedure

As it was not possible to evaporate metal onto a sample positioned at the centre of curvature of the LEED screen without some danger of stray metal hitting the screen a movable shield was installed. This could be positioned across the front aperture of the screen during evaporation but rotated clear during LEED and A.E.S. operations.

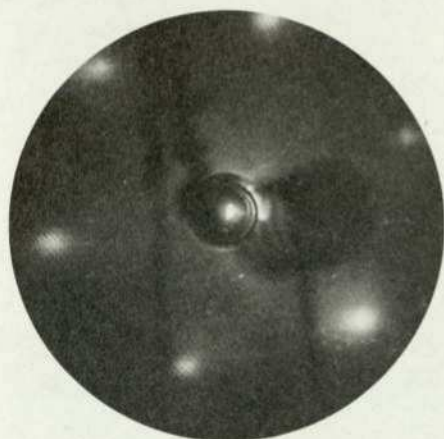
A series of experiments was carried out to ensure that a copper film could be evaporated onto the platinum crystal and detected by A.E.S. The control of evaporation at the sample crystal at the normal rate of 0.003 M-L/sec was found to be unnecessarily fine and entailed frequent

reloading of the source wire. To reduce the frequency of this disruptive process the isolating valve to the evaporation source cross-piece was removed to bring the source nearer the sample and so increase the flux density of evaporated metal. This modification increased the metal deposition rate and total amount by a factor of ~ 5 ; the initial source degassing and first evaporation, which had previously been carried out with the isolation valve almost closed to ensure shielding of the crystal, was then carried out with the sample crystal raised and rotated out of the 'beam' from the source.

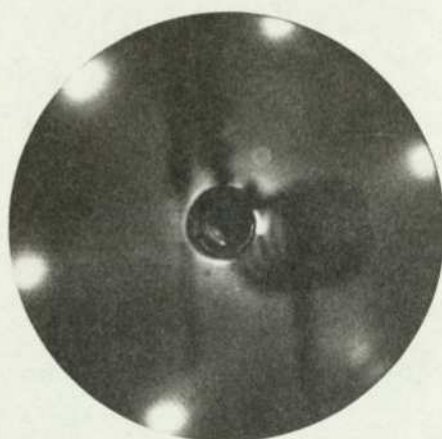
III.4.2.2 Results

III.4.2.2.1 LEED Patterns from Overlayers of Copper on Pt(111)

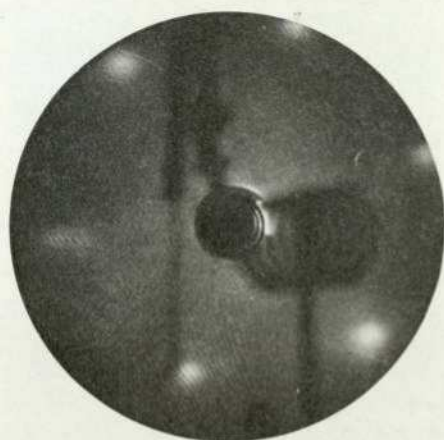
Copper was evaporated from a tungsten wire source at a rate of 0.015 Cu(111) M-L/sec onto the large Pt(111) crystal which had been cleaned by oxidation followed by argon ion bombardment and annealing and allowed to cool to room temperature. The LEED pattern before evaporation was a bright Pt(111)-(1x1), shown in Figure III.13a. After evaporation of 0.16 Cu(111) M-L, the pattern remained a Pt(111)-(1x1)-Cu with a slight increase in background (Figure III.13c). Further evaporation to 0.36 Cu(111) M-L then 0.72 Cu(111) M-L still resulted in a Pt(111)-(1x1)-Cu, shown in Figure III.13d. A copper deposition to a total of 1.1 and then 1.8 Cu(111) M-L gave rise to a diffuse (1x1) of low intensity. The A.E.S. spectra obtained after each evaporation showed the build up of the copper signal with sulphur and carbon as the only significant impurities.



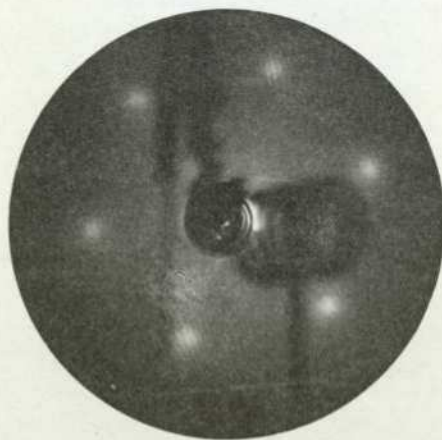
a) 69 V
Pt(111) (1x1)
Clean Surface



b) 60 V
Pt(111) (1x1)-Cu
Annealed Copper Film



c) 66 V
Pt(111) (1x1)-Cu
0.16 M-L Copper



d) 114 V
Pt(111) (1x1)-Cu
0.72 M-L Copper

FIGURE III.13 LEED patterns from Pt(111) + Copper.

Oxygen absorption on the 1.8 Cu(111) M-L film surface made no observed difference to the diffuse Pt(111)-(1x1)-Cu pattern but annealing at $\sim 650^{\circ}\text{C}$ for 15 s returned to a bright Pt(111)-(1x1), Figure III.13b, while copper was still detected by A.E.S.

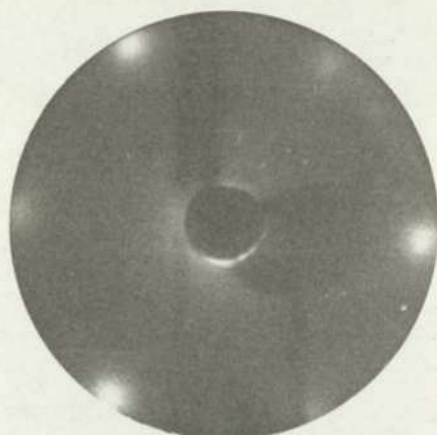
III.4.2.2.2 Heavy copper deposition on Pt(111)

The crystal was cleaned using the standard method (annealing in 2×10^{-7} torr of oxygen at 1000°C for 5 -15 mins, argon ion bombardment for $\sim 4 \mu\text{A}$ - hr. then annealing at 1000°C for 3 - 5 mins). The resulting LEED pattern was a sharp Pt(111)-(1x1), shown in Figure III.14a, with a clean A.E.S. spectrum showing small tin and carbon peaks. This surface was covered with copper by evaporation from the hairpin source. This was operated at a relatively high evaporation rate of 0.1 Cu(111) M-L/sec to an average thickness of 6M-L. The Auger spectrum, Figure III.15, shows carbon as the only appreciable impurity signal in the copper. The LEED pattern, Figure III.14b, was a diffuse f.c.c.(111)-(1x1). To reduce the diffraction spot spacing so that the pattern was observed to fit the LEED screen as before evaporation the electron beam energy was increased from 64 to 69 eV. The surface mesh change was thus $(1-(64/69)^{\frac{1}{2}}) \times 100\%$ decrease. This 3.7% reduction from the Pt(111) surface atom spacing of 2.774 Å to 2.67 Å indicated that the substrate mesh was preventing overlayer growth at the copper spacing at this film thickness.

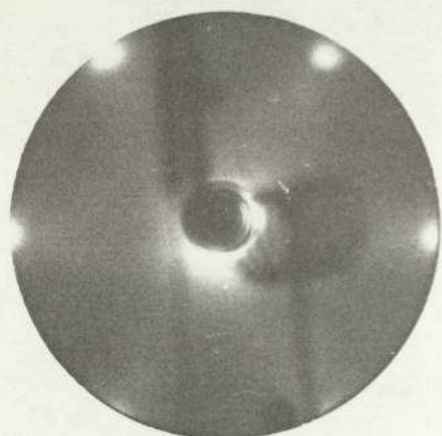
The LEED pattern was unchanged by annealing at 350°C for 20 mins. but the diffraction spots were clearer after annealing at 450°C for 20 mins. Additional, very faint,



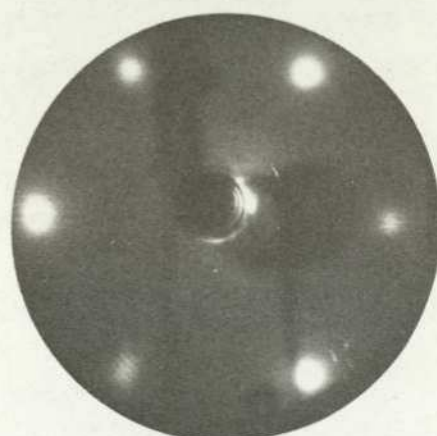
a) 64 V



b) 69 V



c) 62 V



d) 88 V



e) 66 V



f) 66 V

FIGURE III.14 LEED patterns. Heavy evaporation of Copper on Pt(111). a) Clean surface Pt(111) (1x1) b) + 6 M-L Copper c,d) Annealed Copper on Pt(111) e) Before and f) After 3.6 M-L of Copper on Pt(111) at 450°C

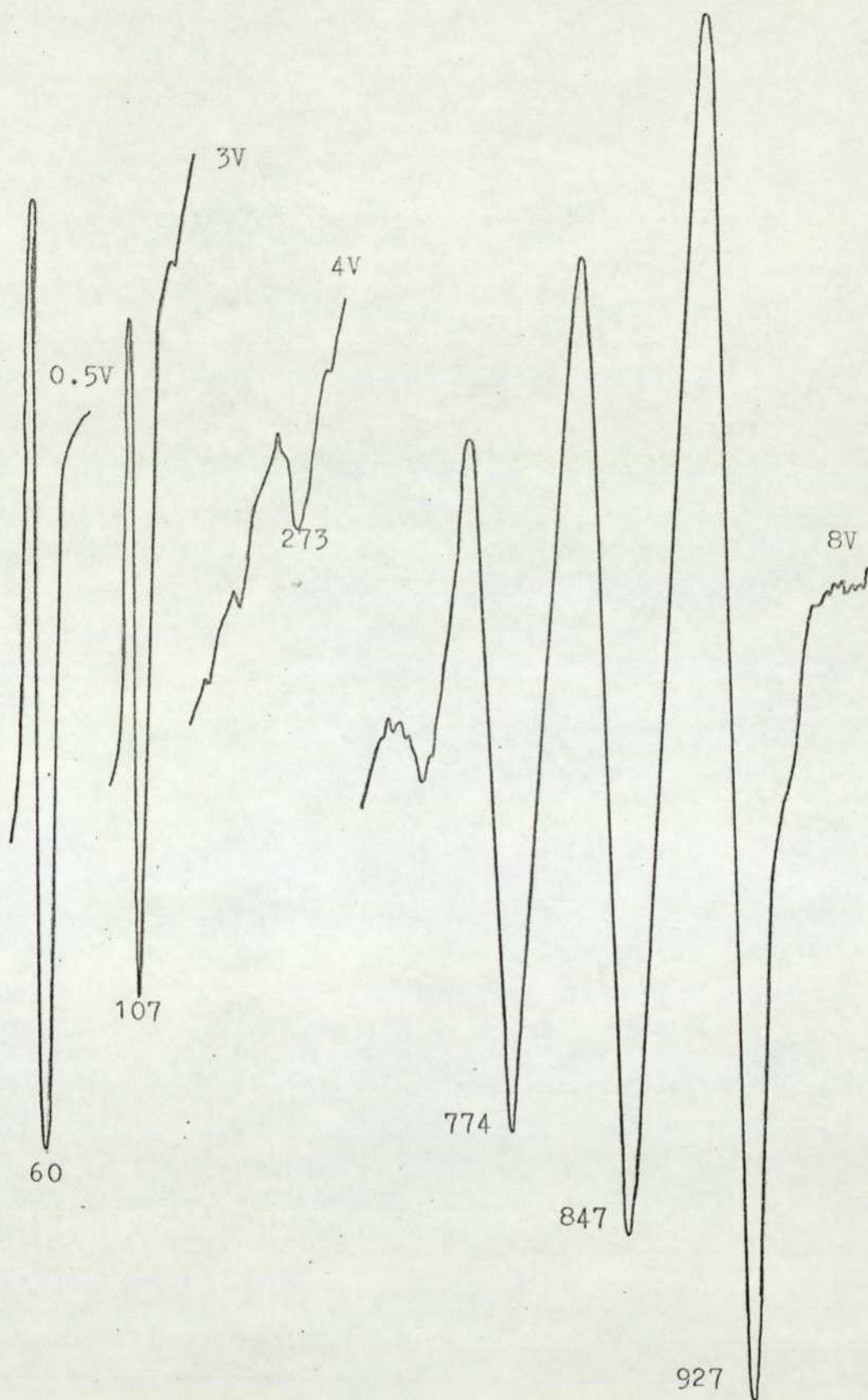


FIGURE III.15 Auger spectrum from 6 M-L of copper on Pt(111)
 Beam $E_p = 2.5$ keV.

streaked diffraction features were detected on the photograph of the pattern. After annealing the crystal at 600°C for 1 min the pattern was a brighter f.c.c.(111)-(1x1) with lower background, Figure III.14c,d. There was some evidence of streaks inside the first order spots (Figure III.14c). The spot spacing indicated a surface mesh close to the copper value of 2.55 Å. The A.E.S. spectrum showed a reduction in the copper signal to that due to an evaporation of 2Cu(111) M-L and the reappearance of the platinum signal.

An evaporation of 2.0Cu(111)M-L on a cleaned crystal surface again produced a slightly diffuse Pt(111)-(1x1)-Cu.

III.4.2.2.3 Copper on Heated Pt(111)

An evaporation of 0.54 Cu(111) M-L onto a cleaned crystal held at 450°C resulted in a bright Pt(111)-(1x1)-Cu, with very little increase in spot size for the same beam conditions before and after evaporation. The A.E.S. spectrum showed a moderate copper signal with the platinum signals reduced (e.g. Pt 151 eV reduced by $\sim 20\%$).

A series of evaporations at a rate of 0.03M-L/sec was carried out onto the cleaned crystal maintained at 400°C . The monitored layer deposition recorded using the quartz crystal for the first evaporation was 1.8 Cu(111) M-L. The background pressure of 2×10^{-10} torr rose to 8×10^{-10} during evaporation. The crystal was kept at 400°C for a further 2 mins. after evaporation. The observed LEED pattern was a sharp f.c.c.(111)-(1x1) with a surface mesh spacing corresponding to Cu(111)-(1x1).

A further evaporation of 1.8 Cu(111) M-L onto the crystal

annealed at 400°C also maintained the Cu(111)-(1x1) surface mesh with an additional trace of Cu(111)-(2x2). This pattern is shown in Figure III.14f. The A.E.S. spectrum showed weak platinum and large copper signals. The surface, at 400°C, was then subjected to another 1.43 Cu(111) M-L evaporation after which a very clear high contrast Cu(111)-(1x1) was observed. The A.E.S. spectrum consisted of very large copper peaks with only a very small 254, 239, 179 and 164 eV peaks from platinum. Carbon and sulphur levels were also very low.

An A.E.S. spectrum was taken of the back face of the crystal to detect if copper evaporated on the front face had diffused to the back; none was observed.

When removed from the vacuum system after no further treatment the surface copper was etched off in high purity nitric acid diluted to 40% which was then analysed using atomic absorption methods. If all copper detected had been etched from the front face of the Pt(111) crystal the deposited copper corresponded to 5.0 Cu(111) M-L (9.2×10^{15} atoms cm^{-2}). This value was used to determine previous monitored depositions as a direct calibration.

The A.E.S. peak sizes for the 3 major copper peaks in the range 700 - 1000 eV and the 239 eV platinum peak were plotted as in Figure III.16.

III.4.2.2.4 Pt(111) - Copper Summary

- 1) Evaporation of up to 2 Cu(111) M-L copper on this face at room temperature caused the Pt(111)-(1x1) clean surface pattern to deteriorate to diffuse Pt(111)-(1x1)-Cu.
- 2) Evaporation at an increased rate caused a more ordered

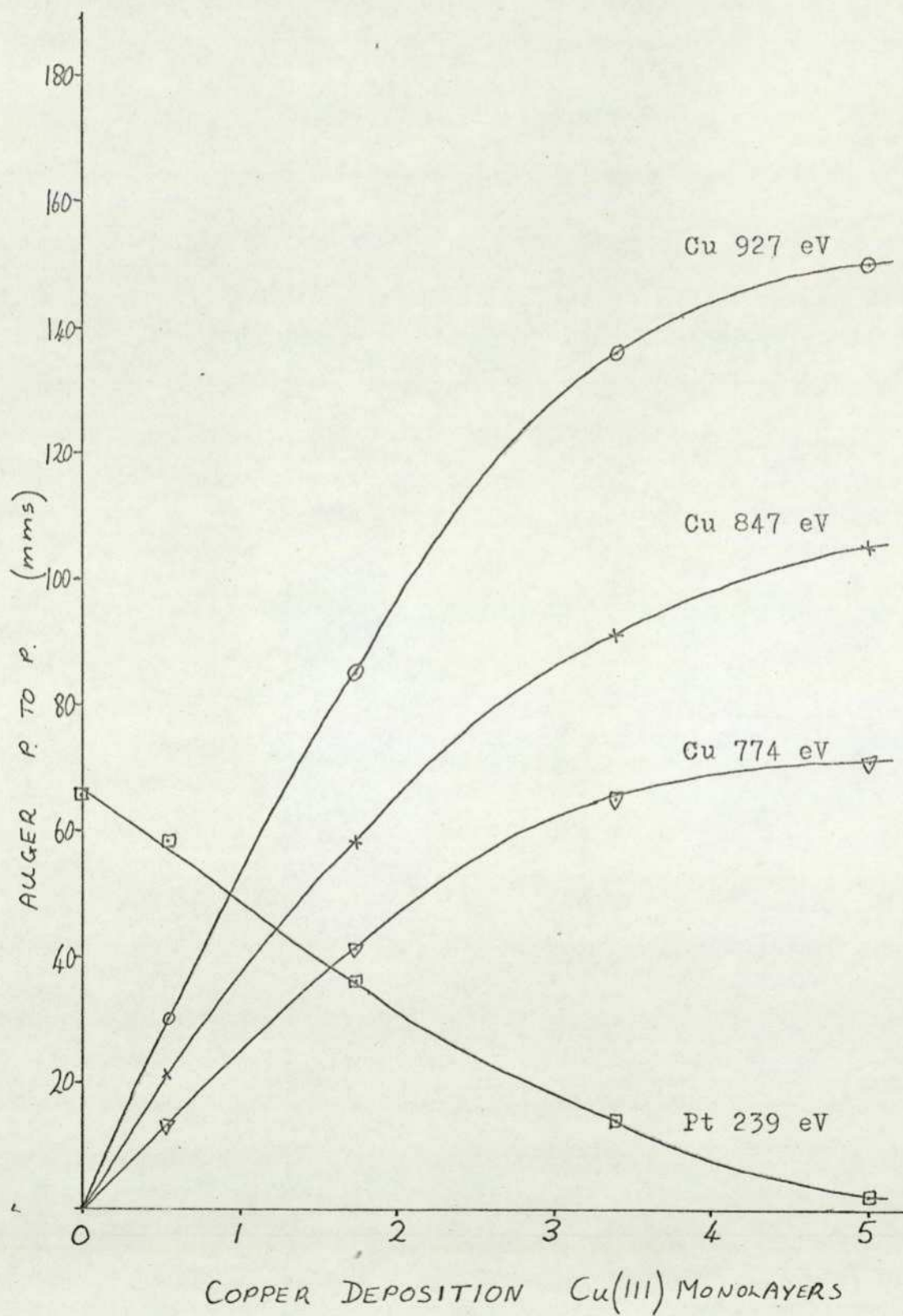


FIGURE III.16 Increase of Copper A.E.S. Peaks.
Copper Evaporated onto Pt(111) at 400°C.

overlayer to form. The reduced diffraction spot size enabled a contraction of surface spacing from that of platinum to be determined.

3) The surface copper formed a layer with bulk copper spacing after annealing at up to 600°C but the copper A.E.S. signal decreased. No clear coincidence mesh diffraction patterns were seen.

4) Clear bulk copper epitaxial growth occurred on the crystal when evaporation was carried out with the crystal at 400°C .

III.5 A Surface Study of Pt(100)

III.5.1 Pt(100) Clean Surface Structure

The first part of the study of the (100) face of platinum was directed towards relating the appearance of the Pt(100)-(5x1) surface structure with the presence of alkali metals, particularly calcium, at the surface. A theory proposed by Edmonds, McCarroll and Pitkethly⁽¹⁾ links the appearance of this pattern with these metals which diffuse near to the surface particularly when the platinum is annealed in oxygen. The work of Grant and Haas⁽⁶⁸⁾, which reports the only procedures by which an apparently clean platinum A.E.S. surface spectrum has been related to a Pt(100)-(1x1) LEED pattern, shows the importance of oxygen treatment in the preparation of a clean surface.

III.5.1.1 Experimental Procedure

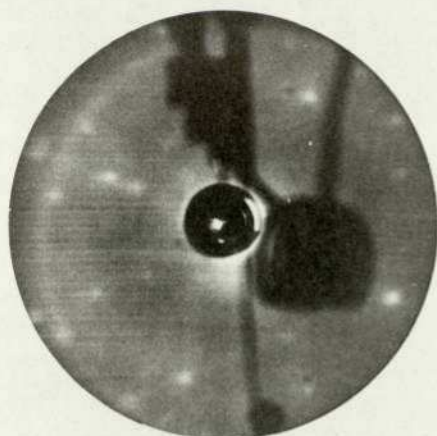
The Pt(100) crystal 6 mm in diameter had been prepared from a 5N purity boule by Metals Research Ltd. using spark cutting

and planing methods and supplied to B.P.(Sunbury) where it had been polished with diamond abrasives and used for LEED and E.S.C.A. studies.

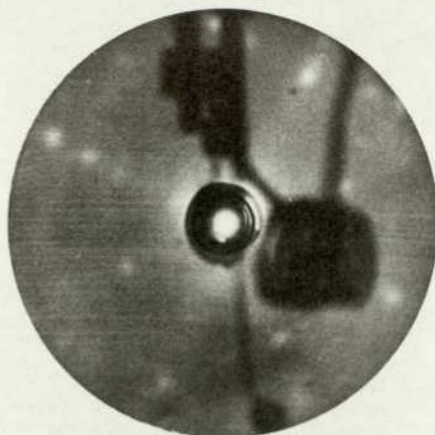
The crystal as received had been examined by E.S.C.A. in a high vacuum system followed by degreasing in trichloroethylene and etching in concentrated sulphuric acid. It was supported on a platinum wire and installed in the LEED/A.E.S. system. The residual pressure after bakeout was 2×10^{-10} torr. The first A.E.S. spectra showed the surface to be covered with carbon with some sulphur, while the only LEED beam observed was a diffuse(0,0) spot in a high background.

After annealing at 860°C for 15 mins to outgas the crystal the surface carbon was found to have taken up a graphite spacing with its characteristic modulated ring pattern. This carbon signal was reduced but not completely removed by a glow discharge of $70 \mu\text{A}$ for 20 mins. Calcium was also present at this stage before any oxygen treatment in the system and without an oxygen A.E.S. peak above noise.

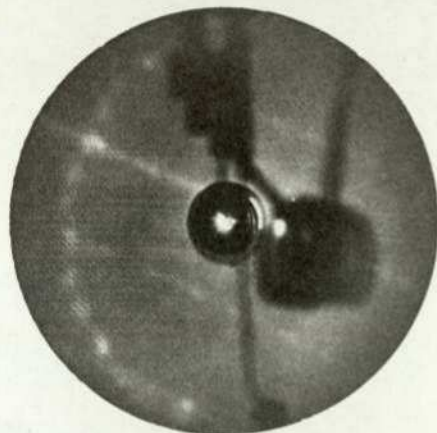
The crystal was then cleaned by annealing in oxygen initially with the ion pump partially throttled but this method allowed excessive build-up of carbon monoxide and left a surface with a mixture of LEED patterns including a faint graphite ring (Figure III.17a). After annealing in oxygen at a lower total pressure but higher purity with no baffle on the ion pump (5×10^{-7} torr of oxygen at 850°C for 4 hrs.) the LEED pattern (Figure III.17b) was again a poor $\text{Pt}(100)-(2\sqrt{2} \times 2)\text{R}45^{\circ}$ but the graphite ring was not ob-



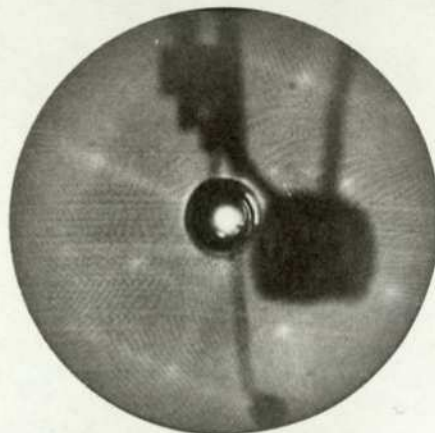
a) 62 V



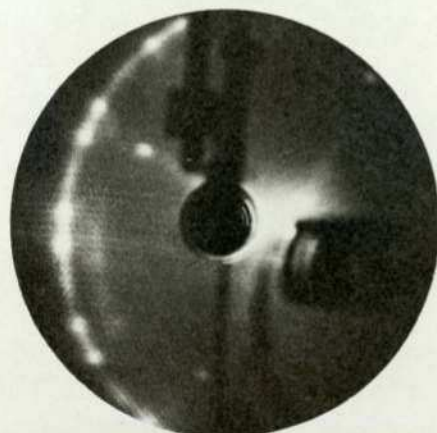
b) 52 V



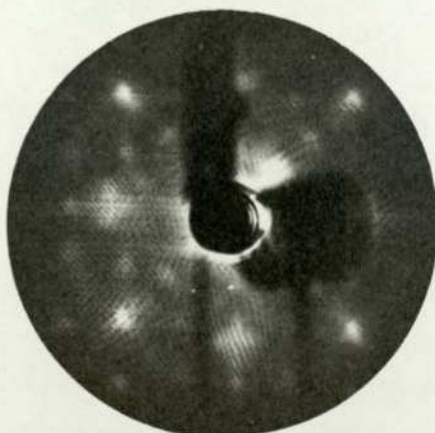
c) 37 V



d) 54 V



e) 44 V



f) 65 V

FIGURE III.17 LEED Patterns from a Pt(100) surface during cleaning treatments. a,b) Major impurity Carbon. c,d) Major impurity Oxygen. e) Surface Carbon after annealing in vacuum only after acid etching.

served. The diffuse spots in the $(n/5, 0)$ positions (n is an integer) characteristic of the $\text{Pt}(100)-(5 \times 1)$ had become clearer.

A prolonged anneal at 800°C for 5 hrs. in 5×10^{-7} torr of oxygen gave rise to the ring LEED pattern of Figure III.17c,d. However, the A.E.S. spectrum taken of this surface showed very large oxygen and small carbon peaks. The calcium level was then very low.

After annealing the crystal in 3×10^{-7} torr of hydrogen for 30 mins. at 920°C the oxygen peak was greatly reduced to about $1/5$ of its previous size and the calcium peak approximately doubled but was still small.

The crystal was removed from the system and etched in cold concentrated, spectroscopically pure sulphuric acid for 3 hours before installing in the system again and pumping down. The surface was heavily contaminated with carbon which ordered to a strongly modulated graphite ring after annealing at 1000°C for 40 mins, - Figure III.17e.

The surface was cleaned sufficiently to allow a $\text{Pt}(100)-(5 \times 1)$ pattern to be observed by the following process:

- 1) Annealed for 2 hours at 1000°C in 5×10^{-8} torr of oxygen
- 2) " " 30 mins " " " 2×10^{-7} torr of hydrogen
- 3) " " 30 mins " " " 4×10^{-9} vacuum
- 4) Argon ion bombarded at $0.7 \mu\text{A}$ and 560 eV for 1 hour
- 5) Annealed for 20 mins at 800°C

The A.E.S. spectrum of the surface resulting from this cleaning procedure is shown in Figure III.18. There are no large signals from impurities. However, the pattern deter-

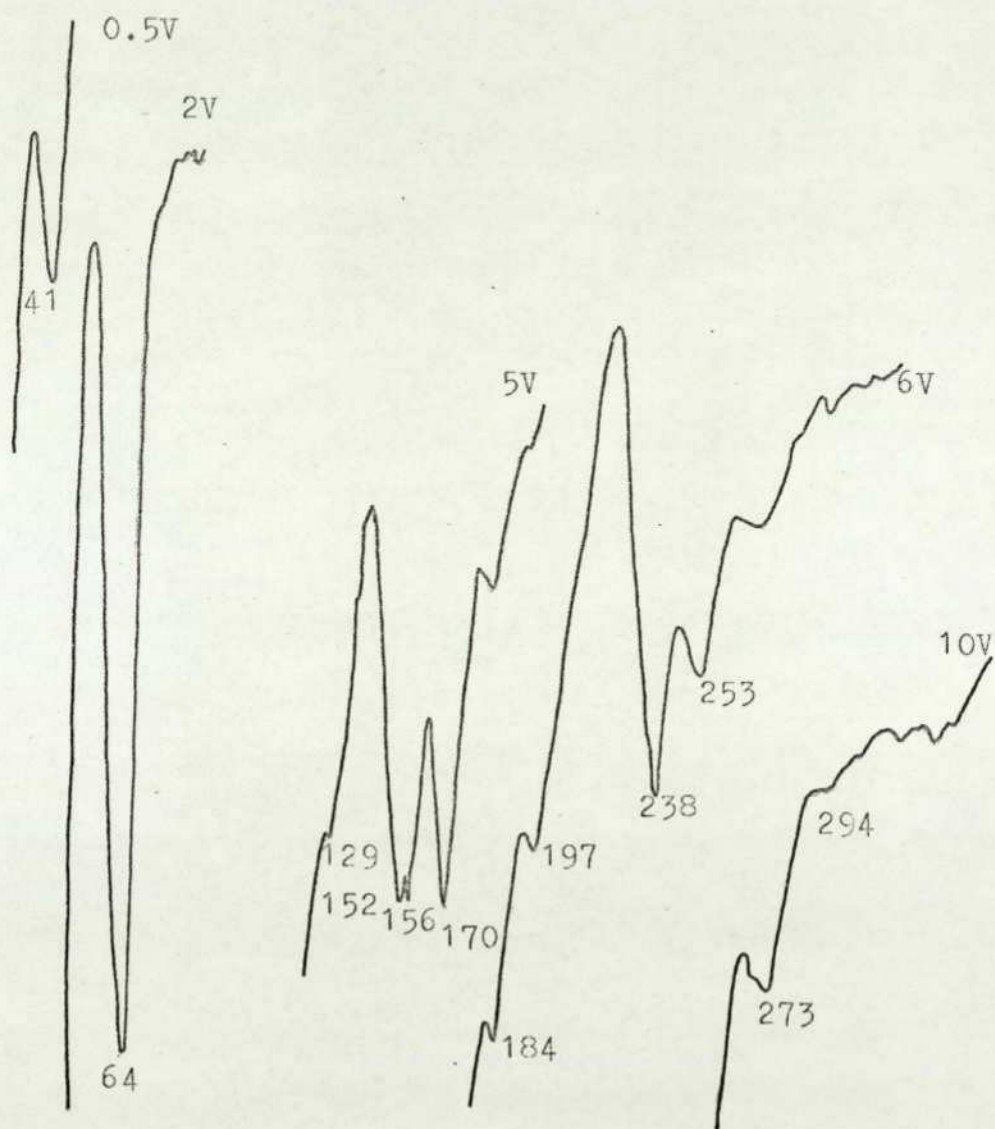


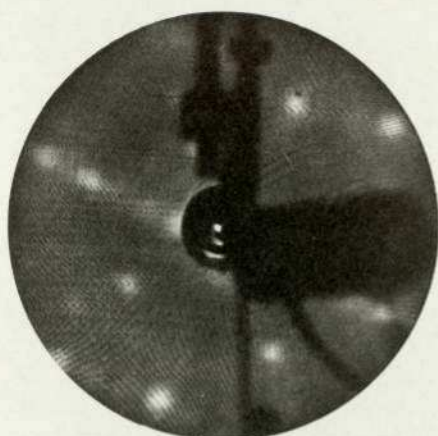
FIGURE III.18 Low impurity levels on Pt(100).

iorated after several hours in a poor vacuum to give a $\text{Pt}(100)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$. (Figure III.19a).

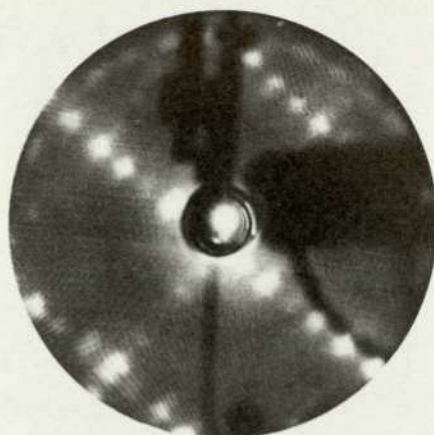
After the crystal had been again removed and etched in dilute boiling, then cold concentrated spectroscopic purity sulphuric acid the cleaning process on reinstalling quickly brought back a surface with $\text{Pt}(100)-(5\times 1)$ features. Two cycles of argon ion bombardment at $1\ \mu\text{A}$ for a total of 100 mins with annealing at 1000°C for 2 mins after each cycle resulted in a $\text{Pt}(100)-(5\times 1)$ LEED pattern (Figure III.19b). The A.E.S. spectrum showed no calcium but small carbon and sulphur peaks. When subsequently annealed at 1050°C , the crystal emitted potassium ions strongly into the mass spectrometer. The poor resolution of the A.E.S. analyser made the potassium 252 eV peak indistinguishable from the platinum 251 eV peak while both were affected by the presence of carbon with its 273 eV peak. After a total of 20 mins. at 1050°C the carbon and sulphur levels were found to have increased and the LEED patterns modified to $\text{Pt}(100)-(5\times 1) + \text{streaked } (2\times 2) + \text{modulated graphite ring}$ (Figure III.19c,d).

The crystal was then annealed in oxygen then hydrogen and argon ion bombarded followed by a second oxygen/hydrogen treatment at 1050°C with gas pressure of 5×10^{-7} torr for $1\frac{1}{2}$ hours. The resulting carbon A.E.S. signal was hidden in the normal noise and the calcium signal was low. However a $\text{Pt}(100)-(5\times 1)$ pattern was again observed.

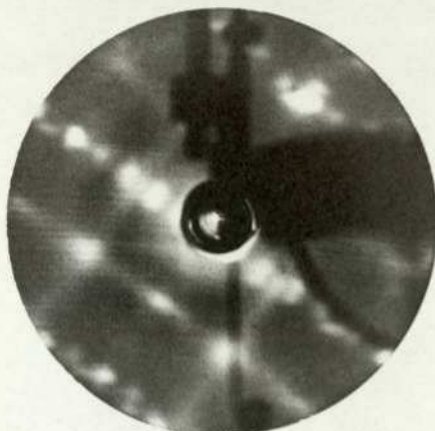
The crystal was again etched in boiling 50% aqua regia for 10 mins then cold high purity sulphuric acid for 20 mins



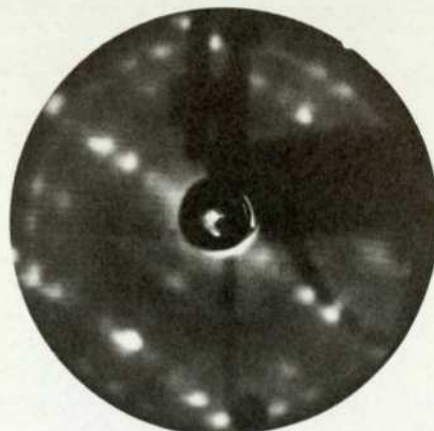
a) 45 V



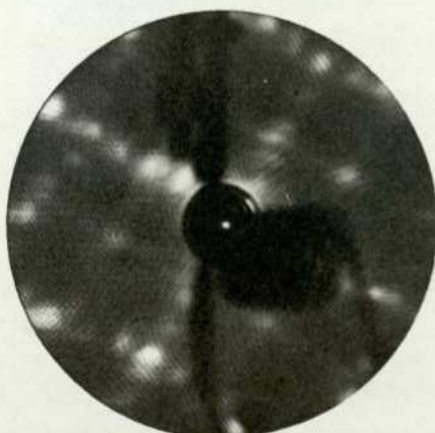
b) 56 V



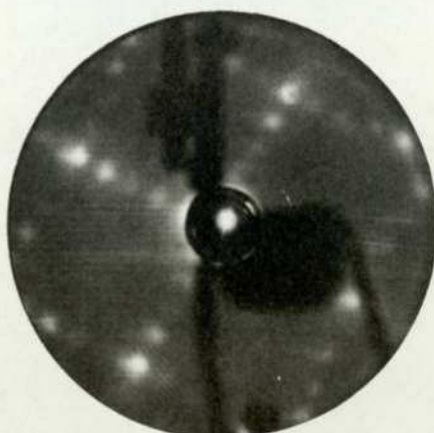
c) 46 V



d) 64 V



e) 45 V



f) 63 V

FIGURE III.19 LEED Patterns from Pt(100) during cleaning. Various impurity patterns coexist with the Pt(100) (5x1).

and washed in distilled water. After installation and bakeout in the system the crystal was found to have large carbon and sulphur A.E.S. peaks. When the crystal was annealed at 1050°C the ion emission to the mass spectrometer was found to be predominately potassium(K^{+}) but sodium(Na^{+}), initially a moderate peak reduced after ~ 100 s. A small calcium(Ca^{+}) peak was also observed.

After argon ion bombardment for a total of 10 μA - hrs the crystal was annealed at 1050°C for 4 mins. The ion emission was again high potassium and low sodium and calcium. The LEED pattern from the crystal when it had cooled to room temperature, shown in Figure III.19f, was a $\text{Pt}(100)-(5 \times 1)$ with a weak graphite ring but with unclear splitting of the $(0, n/5)$ spots. The A.E.S. spectrum of the range 340 - 220 eV is shown in Figure III.20; no calcium was detected.

The crystal was then annealed at 1050°C in 5×10^{-8} torr of oxygen for 20 mins and the LEED and Auger results obtained. The LEED pattern, Figure III.19e, showed a $\text{Pt}(100)-(5 \times 1)$ as in Figure III.19f but with an additional $\text{Pt}(100)-(2 \times 2)$ pattern. From the A.E.S. spectrum the additional pattern appeared to be due to surface sulphur.

The appearance of surface calcium was again observed by A.E.S. on the crystal when it was annealed at 900°C in oxygen at a pressure of 4×10^{-8} torr for 1 hr then annealed at 900°C in vacuum of less than 1×10^{-9} torr for 5 mins. The LEED pattern was a poor $\text{Pt}(100)-(1 \times 1)$.

A separate vacuum system was set up to enable the high temperature/argon ion bombardment cleaning method used by

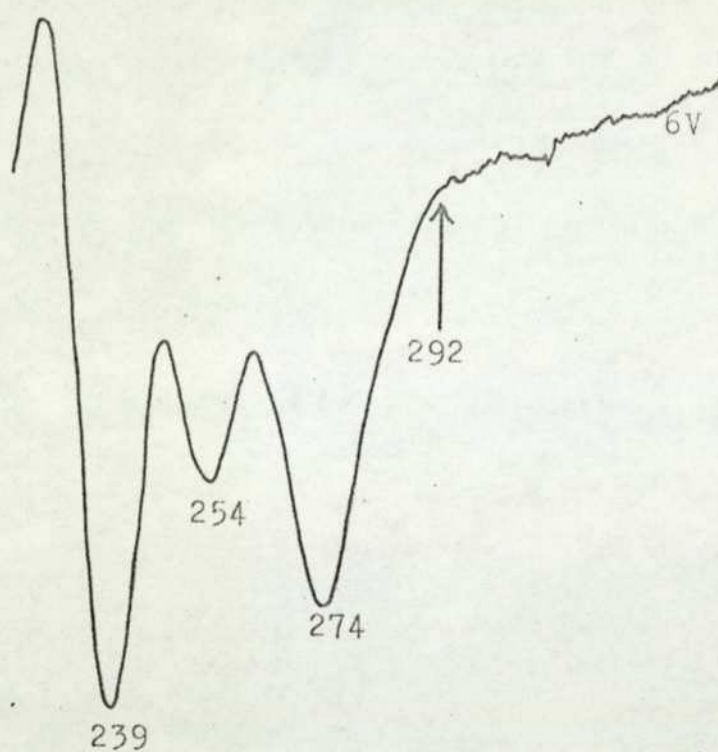


FIGURE III.20 Auger spectrum from Pt(100) crystal which shows the Pt(100)-(5x1) LEED pattern.

Grant and Haas⁽⁶⁸⁾ to be tried. A metal chamber with an observation window could be pumped by a 4" oil diffusion pump through double chevron baffles cooled by water and liquid nitrogen. The ultimate pressure of 1×10^{-8} torr was obtained after a 120°C bake. The Pt(100) crystal was clipped to a 0.25 mm platinum foil strip which was mounted between two terminals of a high current feedthrough and a stainless steel probe wire from the third terminal positioned 5 mm from the crystal front face. This unit was installed in the system and baked to give a pressure on cooling of 1×10^{-8} torr when the pump was throttled and B.O.C. grade X argon admitted via a leak valve. With 300 V maintained between the probe and the crystal the argon pressure was allowed to rise until a glow discharge struck between them. The voltage and pressure were adjusted to give a well localised stable discharge near the crystal (crystal at -200 V with respect to the probe). The crystal was then heated to 1000°C as determined by an optical pyrometer and maintained in the 2.4 mA glow discharge current for 2 hours.

The crystal was then reinstalled in the LEED/A.E.S. system with no further etching. After baking, the crystal was argon ion bombarded for 17 μA - hrs followed by annealing at 900°C for 10 mins whilst pumping down in a vacuum with predominantly residual argon.

The LEED pattern observed after this treatment was a Pt(100)-(5x1) and a graphite ring. The cleaning process had not removed all carbon as reported by Grant and Haas. This was thought to be due to carbon contamination of the

main and gas manifold vacuum systems. After further baking of these components the crystal was again argon ion bombarded for 12 μA - hrs. The resultant diffuse Pt(100)-(1x1) returned to a Pt(100)-(5x1) with a graphite ring on annealing for 250 s at 900°C. The A.E.S. spectrum, which was considerably improved in sensitivity after modifications to the system, showed a moderately large carbon peak.

Almost all of the surface carbon was removed by annealing the crystal for 30 mins in 5×10^{-7} torr of oxygen at 900°C but a large oxygen peak and small sulphur peaks were then observed on the A.E.S. spectrum. No calcium was visible after this treatment. The oxygen and sulphur were easily removed by a short argon ion bombardment (0.2 μA - hr) without bringing calcium to the surface but some surface carbon was then found.

It was obvious that an argon ion gun with high ion current and low contamination used after a heavy oxygen treatment would result in the cleanest surfaces on platinum.

III.5.1.2 Pt(100) - Summary of Results

- 1) The crystal as received was very heavily contaminated by carbon. Extensive cleaning cycles were required to reduce the surface carbon.
- 2) The crystal, showing no surface carbon before removal from the vacuum system was found to be heavily contaminated on reinstallation. This is contrary to the experience of Grant and Haas⁽⁶⁸⁾ and indicated a higher level of system impurities. A higher pumping speed capability for carbon monoxide was required. (Titanium sublimation pumping).

- 3) After etching in high purity acids the Pt(100)-(5x1) pattern could be observed with no oxygen treatment. No calcium was then detected by A.E.S.
- 4) The surface structure after argon ion bombardment was a diffuse Pt(100)-(1x1). The Pt(100)-(5x1) developed after annealing treatment.

The presence of calcium at the surface, as detected by A.E.S., was not related to the appearance of the Pt(100)-(5x1) diffraction pattern.

Surface calcium was detected after annealing following recent oxygen treatment.

Potassium and sodium, emitted as ions at high temperatures and observed by mass spectrometry were difficult to detect by A.E.S. at 300°C. Pt(100)-(5x1) occurred both when little contamination was detected by A.E.S. and, less clearly, when high levels of sulphur and carbon were present.

The emission of alkali metal ions from the heated crystal was qualitatively unaffected by surface cleaning.

III.5.2. Evaporation of Copper on Pt(100)

This work was divided into two sections; a) the LEED study of the growth of copper evaporated onto Pt(100) and the limits of pseudomorphic growth b) the A.E.S. response to increasing deposition of evaporated copper. It was found that the two approaches were not independent. The experiments which showed that the Auger response depended on the surface structure detected by LEED are also described.

The errors of surface mesh determination using LEED

depended on the reproducibility of crystal positioning in the system. To overcome this source of error when determining the limits of pseudomorphism of copper growth on Pt(100) a method of evaporating over only half of the crystal face was used. The pattern from the overlayer could be compared with that of the clean surface by a very short vertical shift of the crystal using the manipulator.

Prior to inserting the crystal into the vacuum system the crystal face was made perpendicular to the plane of the LEED electron gun. This was achieved by supporting the crystal manipulator with the axis of rotation vertical. A reference mark was then positioned in a bench clamp at a distance of 3 m from the manipulator so that it was on the sight line taken across the mating face of the manipulator flange. A small bright light source was then supported vertically above the reference mark at the same separation from it as the crystal/flange distance. The crystal support wires were then tweaked until the reflection of the light source in the crystal face was centred adjacent to the light source. This position was checked for minimal precession of the crystal face about the rotation axis. When installed a vertical movement of the manipulator caused no change in the position of the source of diffracted beams relative to the fluorescent screen.

The crystal was cleaned using the standard method of oxygen annealing, argon ion bombardment and vacuum annealing. Several cycles of this treatment were needed to clean the crystal after installation in the vacuum system. Subsequent-

ly, the oxygen treatment was omitted if very little carbon was observed by A.E.S. and just argon ion bombardment followed quickly by a short anneal at $\sim 1000^{\circ}\text{C}$ was used. The system residual pressure with the LEED or A.E.S. guns operating was 2×10^{-10} torr and this rose to 1×10^{-9} torr during operation of the wire copper evaporation source. The normal evaporation rate from this source was maintained at 0.02 Cu(100) M-L/sec.

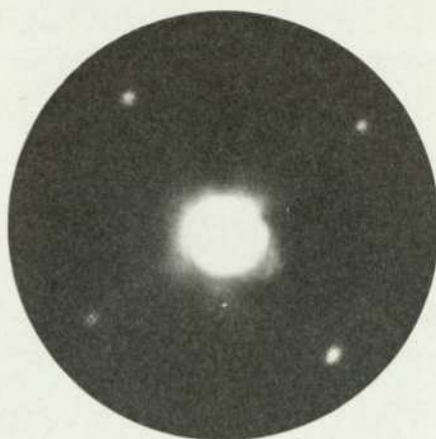
The LEED patterns and A.E.S. spectra from a series of deposited films and adjacent clean surfaces were obtained in the range 0.1 to 5.0 Cu(100) M-L. The maximum quantity was limited by the capacity of the wire source.

For all depositions in this range on a Pt(100) surface at room temperature the cleaned surface Pt(100)-(5x1) pattern was altered to a Pt(100)-(1x1), the normal primitive f.c.c. (100) surface pattern. Examples are shown in Figure III.21a,b corresponding to 1.0 and 0.25 Cu(100) M-L respectively. Figure III.22 shows two pairs of LEED patterns from adjacent areas on the substrate. Surface mesh spacings were determined by superimposing the negatives of such pairs of photographs. Any deviation from identical spacing was noted.

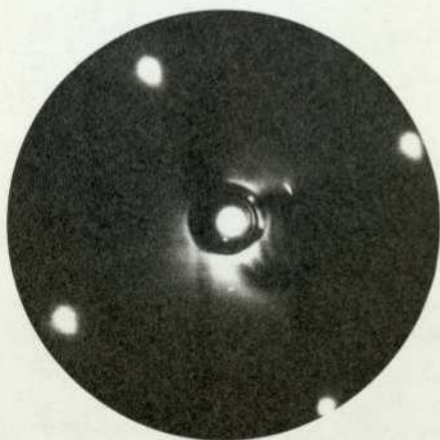
When a series of evaporations had been made over the entire face of the crystal it was removed and etched and the surface coverage of copper determined by Atomic Absorption. By this method the copper deposition was found to be 0.36 of that determined by the initial calibration and calculation assuming point source emission from the wire source.



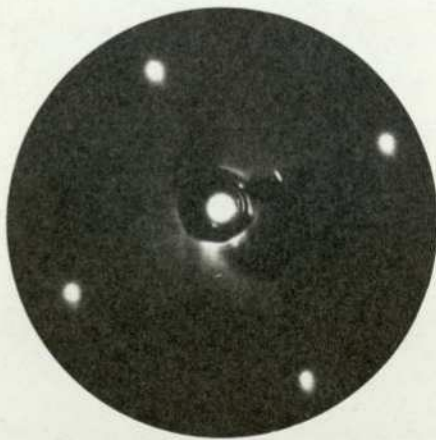
a) 44 V
1.0 M-L Copper
Pt(100) (1x1)-Cu



b) 66 V
0.25 M-L Copper
Pt(100) (1x1)-Cu

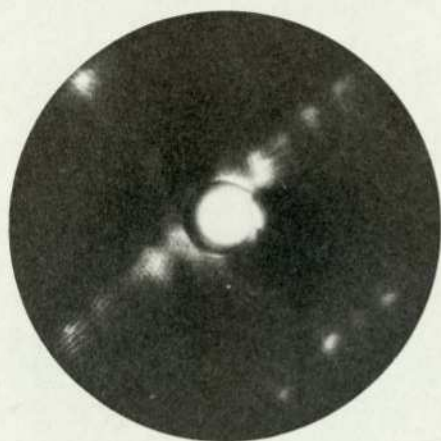


c) 50 V
1.4 M-L Copper
Pt(100) (1x1)-Cu

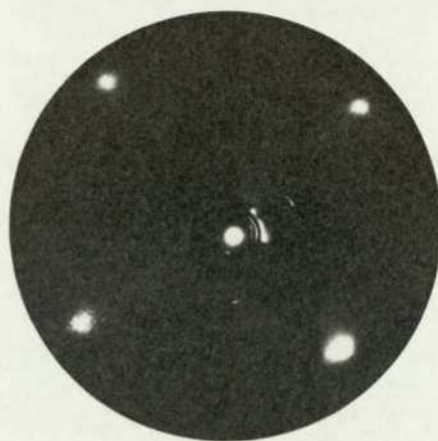


d) 60 V

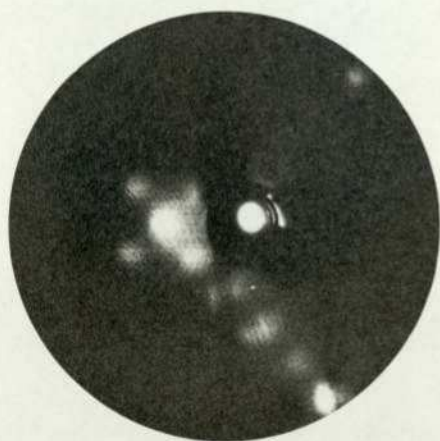
FIGURE III.21 LEED Patterns from Pt(100) with Copper overlayers.



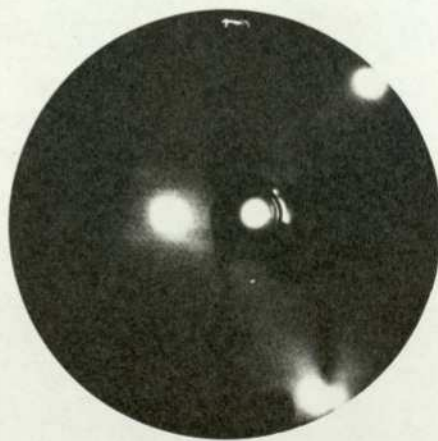
a) 57 V
No Copper
Pt(100) (5x1)



b) 57 V
Copper overlayer
Pt(100) (1x1)-Cu



c) 35 V
No Copper
Pt(100) (5x1)



d) 35 V
Copper overlayer
Pt(100) (1x1)-Cu

FIGURE III.22 Pairs of LEED patterns from a Pt(100) crystal with half of the surface covered by Copper.

For all evaporation within the capacity of the source i.e. up to ~ 5 Cu(100) M-L the surface mesh determined by LEED was a Pt(100)-(1x1)-Cu. When evaporation was carried out in stages with long delays between evaporations of hours or overnight a faint Pt(100)-($\sqrt{2} \times \sqrt{2}$)R45⁰ was observed.

III.5.2.1 Experiment Showing Importance of LEED Pattern in Quantitative A.E.S.

An experiment was carried out in which copper was evaporated onto a dirty Pt(100) surface. After insertion into the system the surface had been annealed at 1000°C in oxygen at 2×10^{-7} torr for 15 mins., but this was insufficient to fully clean the surface. The A.E.S. spectrum showed impurities with small peaks due to oxygen, tin and calcium and a moderate sulphur peak. The LEED pattern was a clear Pt(100)-(2x2)-S and is shown in Figure III.23 (spark marks are due to static on film).

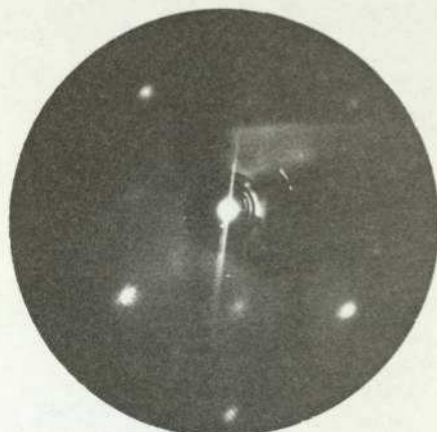
Copper was then evaporated onto the crystal in 3 stages to bring the total coverage as determined subsequently by Atomic Absorption to 7.5 Cu(100) M-L. After the first coverage of 1.8 Cu(100) M-L the LEED pattern was a Pt(100)-(1x1) (Figure III.23b), while the A.E.S. showed the same impurities in addition to copper and platinum. A second deposition of 2.0 Cu(100) M-L on top of this surface resulted in a Pt(100)-(1x1) with a fainter Pt(100)-($\sqrt{2} \times \sqrt{2}$) LEED patterns (Figure III.23c). A final deposition to give a total film thickness of 7.5 Cu(100) M-L gave a surface mesh with a diffuse LEED pattern of Pt(100)-(1x1), Figure III.23d. The A.E.S. spectrum was taken for this surface and the series



a) 79 V



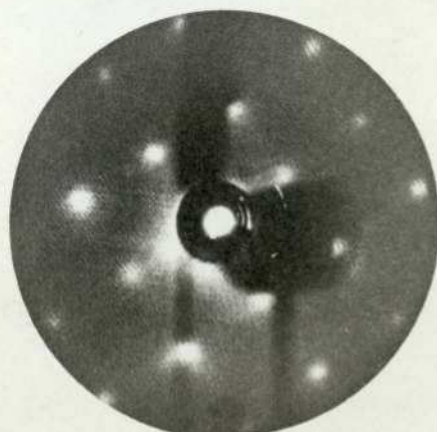
b) 79 V



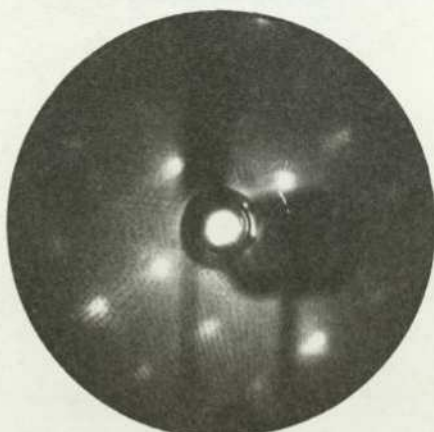
c) 79 V



d) 79 V



e) 54 V



f) 79 V

FIGURE III.23 LEED patterns from increasing coverages of Copper on uncleaned Pt(100).

- | | |
|--|-----------------------------|
| a) Pt(100) (2x2)-S | b) Pt(100) (1x1)-Cu |
| c) Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-Cu | d) Pt(100) (1x1)-Cu diffuse |
| e,f) Pt(100) (2x2)-Cu/S | |

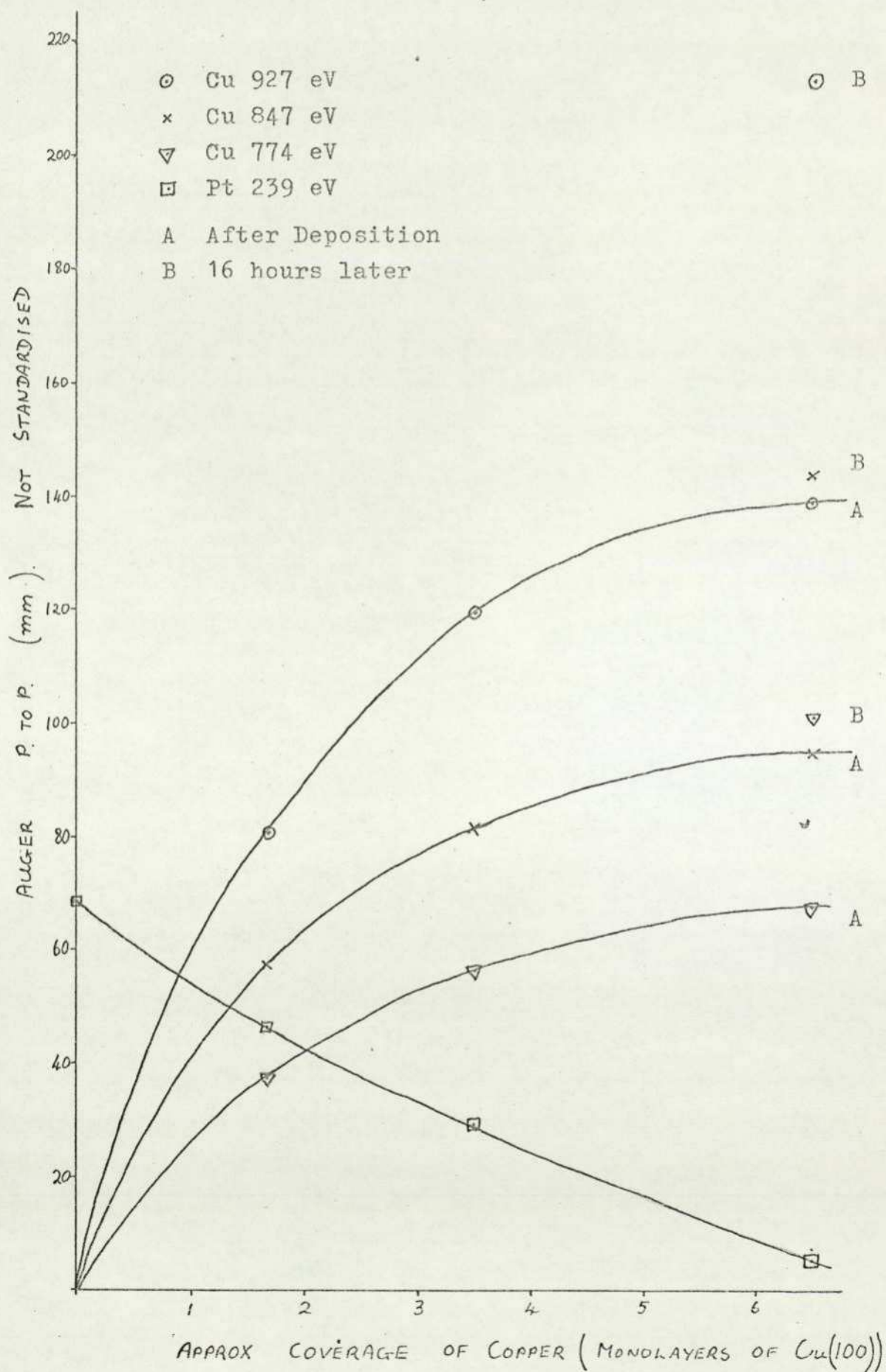


FIGURE III.24 Copper deposition on unclean Pt(100).

showing the build up of copper peaks plotted as in Figure III. 24. However the spectrum taken under identical gun and analyser conditions with the sample unmoved, 16 hours later, showed much larger copper peaks. The corresponding LEED pattern was found to have reverted to a bright $\text{Pt}(100)-(2 \times 2)$, Figure III.23e,f, at the same spacing as the original (2×2) . The crystal was then removed to obtain the calibration of film thickness by Atomic Absorption.

III.5.2.2 Quantitative A.E.S. of Copper on Pt(100)

Uncertainties in previous results were reduced by the following methods:-

a) Use of a high capacity copper source.

The can source could be loaded with sufficient copper to complete a calibration up to at least 12 $\text{Cu}(100)$ M-L. This enabled a cleaner vacuum system to be maintained and the Auger spectrometer system operated without the disruptive process of dismantling for bake-out.

b) Forward direction evaporation monitoring and calibration.

Errors associated with forward evaporation and monitoring behind the source with use of the inverse square relationship for film thickness at a distance were removed by positioning the monitoring quartz crystal slightly off the line to the target. The frequency shift of this crystal was calibrated against copper deposition on a platinum foil at the same position as the crystal in the LEED/A.E.S. system.

c) Crystal surface roughness effects.

The axis of the port used for the glancing incidence A.E.S. gun was measured using a light beam (He/Ne laser)

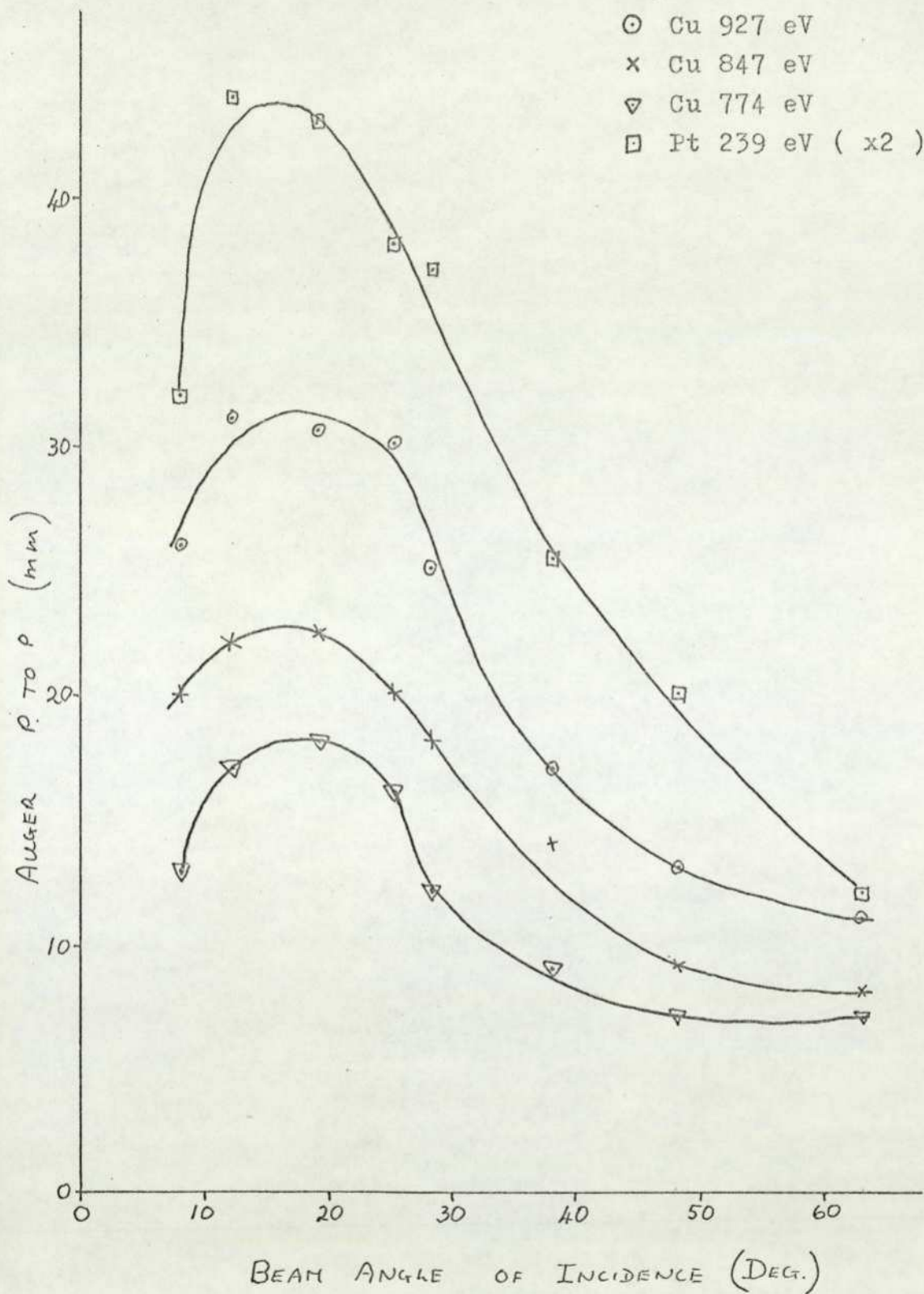


FIGURE III.25 Effect on Auger peak sizes of rotating crystal to alter beam angle of incidence (and collection conditions).

and found to intersect a crystal face, which was normal to the LEED grid axis, at an angle of 12° . This low angle made the A.E.S. spectra highly dependent on surface roughness. Maximum response to copper films by this system was found to occur at an incident electron beam angle of between $15-20^{\circ}$ (Figure III.25). For this quantitative work the angle was standardised at 20° . When determining the angle of the glancing incidence A.E.S. gun pot^r the point where the light beam, passing down the port axis and through the centre of curvature of the LEED grids and screen, intersected the R-F coil just beyond the crystal was noted.

For A.E.S. work this crystal was raised above the screen centre of curvature and the glancing incidence electron beam moved, using the gun X and Y deflection plates, until the light spot where the beam hit a surface was moved to the position on the R-F coil which indicated that the beam was passing through the centre of curvature of the screen. The crystal was then moved down and across until it uniformly obscured the LEED electron gun snout when viewed through the centre point of the viewing window. The final positioning in the third direction was made by moving the crystal to or from the screen until the two positions were found at which the illumination of the screen ceased as the beam passed off the crystal at either side. The crystal was then returned to the midpoint of these two positions.

The angle of incidence was then set by rotating the crystal from a position of very low angle of incidence to higher angle until the Kikuchi type channelling patterns

observed on the screen became symmetrical about the screen. This position had been determined as an angle of incidence of 12° . The calibrated manipulator head reading was noted and the rotation continued a further 8° to give a total angle of 20° . By always rotating anticlockwise from low to high angle of incidence prior to A.E.S. the backlash of the manipulator was avoided.

d) Standardisation of Auger Spectrometer.

The electron gun was operated under constant conditions with a beam energy of 2.5 KeV, focussing electrode at -620 V relative to earth and filament can at filament potential. The beam current was maintained constant by running the filament at a current adjusted to give an emission to the can of 0.94 mA; this gave a beam current to the crystal of 60 μ A when the crystal was biased to +470 V to collect most secondary electrons.

The A.E.S. analyser was set up according to the manufacturer's instructions to standardise the input to the phase sensitive amplifier. The standard reference frequency to the amplifier was taken as 2366 Hz and was checked with a RACAL frequency meter before each set of spectra. It was found to be within ± 1 Hz except on occasions when a faulty switch caused a shift of >20 Hz. This frequency was near to the design frequency of 2375 Hz but did not give rise to mains pick up interference. The circuit which had been designed by the manufacturers to maintain a potential of +250 V on the fluorescent screen/collector had been found to drop to below 100 V on load i.e. when a secondary electron current was

collected to allow loss of Auger electron current by secondary emission from the screen. This was modified to maintain at least +200 V on the screen. This improvement is discussed in section II.2.4.

The phase sensitive amplifier was set to 10^{-10} amps f.s.d. and operated with a 1.8 s time constant (Bandwidth 1). The ramp generator was set to give 0.75 V/sec scan rate over two ranges from 1000 V to 500 V and 540 V to 40 V.

The X-Y recorder was matched to the output from the amplifier so that a full scale excursion in each direction, i.e. 2×10^{-10} amps, filled the recorder paper (180 mm) in the Y direction.

e) Film contamination during deposition.

The can source required considerably more heat dissipation during evaporation due to its larger size than the hairpin wire source and gave rise to more gas during evaporation. Evaporation from a newly loaded source caused the system pressure to rise to 2×10^{-7} torr but prolonged outgassing at a power just below that required to give appreciable evaporation reduced outgassing during subsequent evaporations to give a system pressure of $<1 \times 10^{-8}$ torr. The evaporation rate from this source was high, 0.1 to 1.0 Cu(100) M-L/sec, and so produced high purity films despite the poor pressure.

III.5.2.2.1 Stability of A.E.S. spectra; instrument errors.

The quantitative use of A.E.S. required adequate stability of the system when analysing a surface of unchanging composition. The Auger current at an electron energy was taken

as proportional to the peak to peak excursion of the differential energy distribution when operating under standardised conditions. The conditions used in this work are detailed in section III.5.2.2.

The parameters which were most subject to variation in the system irrespective of the surface studied are listed here:

- 1) Beam current. The Auger signal is directly proportional to the incident electron beam current. For the filament used for the work described here the emission to the filament can was kept constant at 0.94 mA. Except under conditions of severe poisoning of the filament the emission to a sample biased at +470 V was then $60 \mu\text{A} \pm 1 \mu\text{A}$.
- 2) Beam angle of incidence. The beam angle of incidence was set at $20^\circ \pm 1^\circ$ by the method described in section III.5.2.2. From the response curve of Figure III.25 the associated error for the copper and platinum peaks shown was a range of 3% of peak height.
- 3) Retarding Field Analyser. The resolution and transmission of the grid system were dependent on the trajectory of the electrons through it. Deviations caused by spurious electrostatic and magnetic fields were kept constant by operating with all electrodes at constant potentials for each spectrum and ion gauges and guns earthed. The trimming magnet, which had been used to move the electron beam onto the crystal, was found to vary the resolution and transmission. A fixed position was found giving least magnetic degradation and all further beam movements made using the gun X-Y scanning plates.

- 4) Amplifier response. The amplifier response was found to be constant within 2% using the internal standard unless the system was seriously disturbed mechanically. This standardisation was described by the manufacturers.
- 5) Beam energy. The beam energy was maintained at 2.5 keV for maximum excitation of the higher energy copper peaks.
- 6) Grid modulating voltage. Each Auger peak was normally obtained at a standard modulation voltage giving maximum signal to noise ratio with sufficient resolution. The dial mark value is shown on all spectra but is related to true modulation voltage in Figure III.26. The dial setting could be reproduced to a 2% level of modulation.
- 7) Chart recorder display. The spectra were recorded with a Y-channel accuracy of $\pm 2\%$.

III.5.2.2.2 Errors Measured Experimentally

4 samples were tested for experimental repeatability. The first two were thought to be stable in U.H.V. for several days.

- 1) Clean platinum. A cleaned Pt(100) crystal was analysed using the A.E.S. system in the standard mode. The Pt 239 eV peak was found to be stable within 5% over a period of 3 days. The apparently large 152 and 254 eV peaks were not taken as a measure of repeatability as they were subject to sulphur 150 eV and carbon 273 eV peak interference.
- 2) Low coverage copper (~ 2 M-L) evaporated onto a room temperature Pt(100) crystal. This was also stable within 5% over 3 days for the 3 low resolution high energy copper peaks and the substrate Pt 239 eV peak.

3) High coverage copper evaporated onto a Pt(100) crystal which was maintained at 400°C. This was stable to within 8% over 20 hours. This additional variation was thought to be due to loss of copper from the surface under the influence of the Auger electron beam.

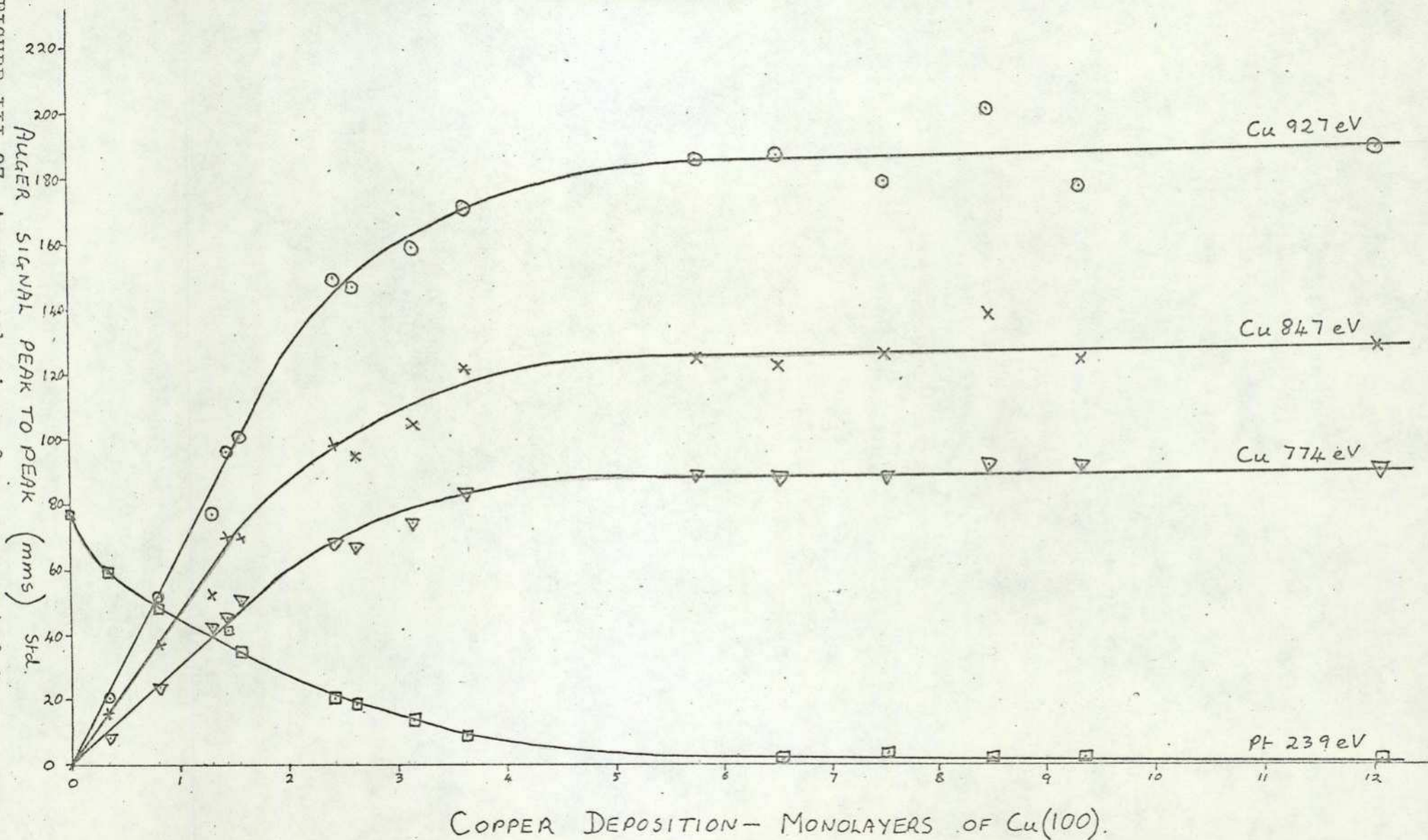
4) Copper coverage (>3 M-L) evaporated onto a room temperature crystal. In this case the Auger response varied widely. This was investigated further and is described in section III.5.2.4.

III.5.2.2.3 Results of Quantitative A.E.S. Copper on Pt(100)

An initial series of evaporations from the can source was carried out on the cleaned Pt(100) crystal which was at room temperature during evaporation and raised to 300°C by the A.E.S. electron beam for each spectrum. The results are shown in Figure III.27 as plots of the peak to peak amplitude of the differential of the Auger electron energy distribution of the 3 major copper features observed in the normal low resolution mode of the analyser. The decrease of the Pt(239 eV) peak was also plotted. Further points were added from later evaporations measured under the standard conditions prior to the gas adsorption studies. This graph does not include measurements from spectra obtained after annealing the crystal above 350°C or where surface impurities were found to be present. The anomalous A.E.S. result described in section III.5.2.1 was found to be qualitatively repeatable in copper films of over 2.5 Cu(100) M-L. Where no major impurity was present the A.E.S. spectra were

FIGURE III.27 Auger peak sizes from evaporated Copper films.

184



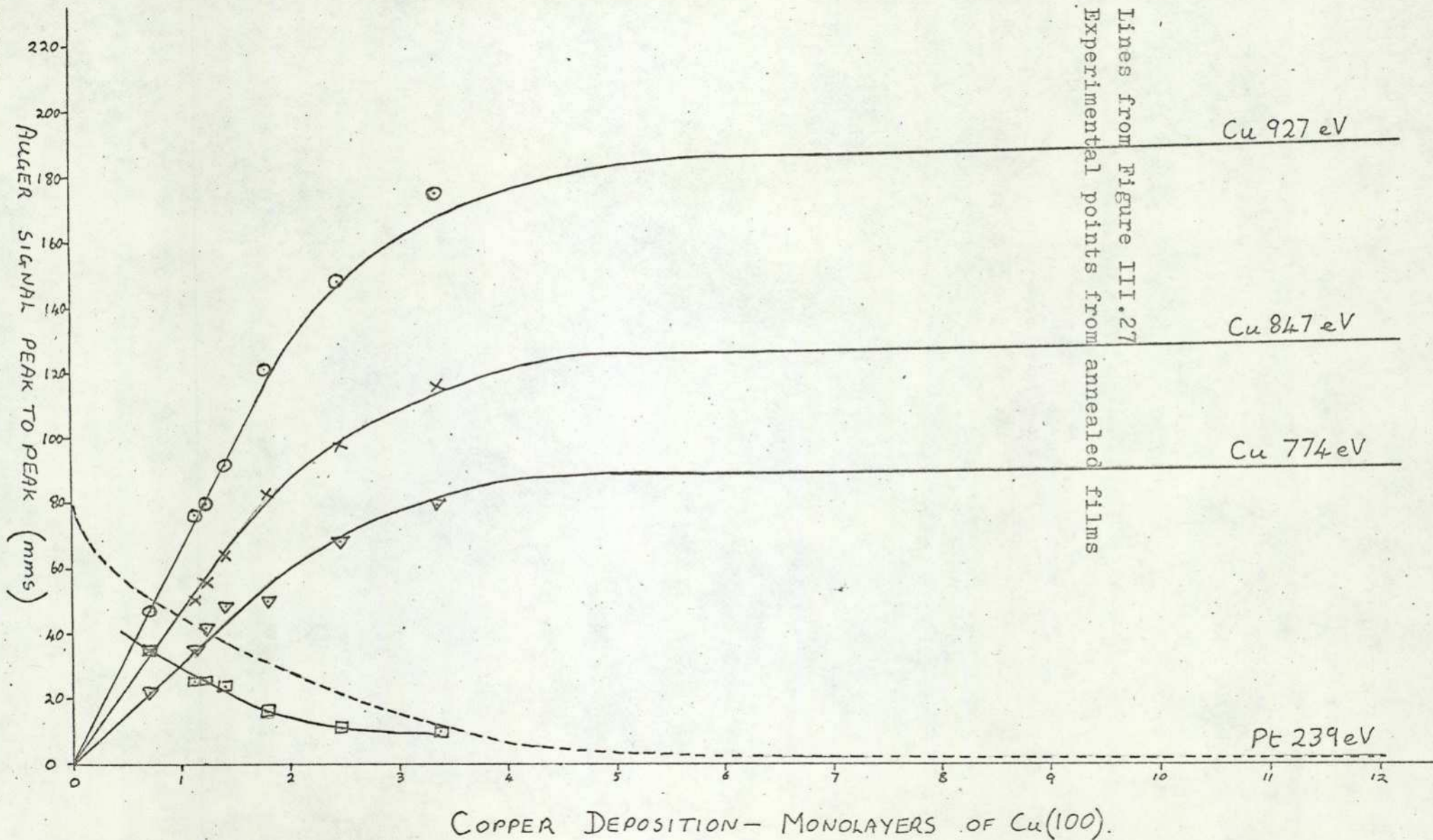
repeatable within $\pm 5\%$ after 2 hours in the A.E.S. electron beam or after being left in vacuum overnight. However, where impurities of oxygen or sulphur were present at the surface, the spectra moved considerably from this calibration to give larger copper peaks.

The LEED patterns from the surfaces used for the calibration were sharp Pt(100)-(1x1) for coverages to ~ 3 Cu(100) M-L when diffuse f.c.c.(100)-(1x1) with faint f.c.c.(100)-($\sqrt{2} \times \sqrt{2}$)R45 $^\circ$ patterns were formed. Ordering to a sharp Pt(100)-($\sqrt{2} \times \sqrt{2}$)R45 $^\circ$ or a Pt(100)-(2x2) was associated with surface impurities and anomalous A.E.S. response.

III.5.2.3 Annealing Copper Overlayers on Pt(100)

Several copper surface films were treated by annealing in the range 400 $^\circ$ - 600 $^\circ$ C before obtaining an A.E.S. spectrum. These spectra showed lower copper peak sizes from those expected for the initial copper deposition quantity (Figure III.27). If the effect of annealing was to reduce the surface copper in an exactly reversed manner to the growth mechanism during deposition then Figure III.27 could be used as a calibration graph for surface copper concentration. In Figure III.28 the lines from Figure III.27 are shown with various experimental points of copper and platinum A.E.S. peak sizes from annealed surfaces. The points are placed arbitrarily in the copper thickness direction so that the copper peak sizes lie on the calibration lines for copper. This positioning allows the platinum peak size points to lie off the platinum calibration line. This failure of peak sizes from annealed surfaces to match those from cold

FIGURE III.28 Auger peak sizes from annealed films



deposited surfaces indicates a different copper surface structure. These results are discussed further in section IV.5.3.

III.5.2.4 Anomalous A.E.S. Response to Copper on Pt(100)

As has been described earlier the A.E.S. response to thin (<3 M-L) films of copper on the Pt(100) crystal was repeatable to $\pm 5\%$ on leaving in vacuum for many hours. For thicker films the response was only stable with time when no significant impurities were present. The maximum change in response, an increase in copper high energy and 107 eV peaks of 53%, was found on the 6.5 M-L copper deposition on an oxygen and sulphur contaminated Pt(100) surface exhibiting a Pt(100)-(2x2). The increase in response which occurred after leaving the sample in vacuum ($<3 \times 10^{-10}$ torr) overnight at 20°C was accompanied by a change in the LEED pattern from a diffuse Pt(100)-(1x1) to a sharp Pt(100)-(2x2).

The importance of oxygen in this process was confirmed in an experiment in which a 9.3 M-L copper film evaporated onto a cleaned Pt(100) surface was treated with oxygen at 6×10^{-8} torr to give an exposure of 70L. A pair of standard conditions A.E.S. spectra was taken before and after this treatment and only showed the appearance of the oxygen peak. The sample was then left overnight at 20°C after which the A.E.S. spectrum was recorded without the crystal being moved and with the electron beam suppressed until the scan approached the copper peak energy position to limit sample temperature rise to $<80^\circ\text{C}$. The copper peaks were then found to be increased by 23% from the initial spectrum. The LEED

pattern from the surface before oxygen exposure was a diffuse Pt(100)-(1x1) which changed to a diffuse Pt(100)-($\sqrt{2}\times\sqrt{2}$)R45°, Figure III.29c, after the oxygen treatment. When left, the pattern changed to a slightly sharper Pt(100)-(2x2) corresponding to the increased A.E.S. copper signal.

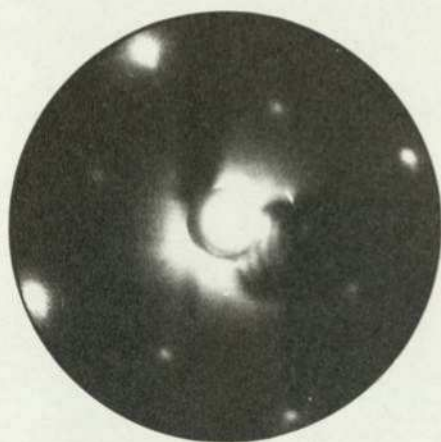
Further prolonged annealing at 300°C by the electron beam for many hours caused a slow decrease in the copper A.E.S. signal levels until they were below the original level after 6 hours. The LEED pattern strengthened to a clear Pt(100)-(2x2). A very small A.E.S. sulphur peak was present throughout the treatments.

A 3.2 M-L film of copper deposited in an atmosphere of 1×10^{-7} torr of oxygen showed the same instability of A.E.S. response with time. The initial deposition gave A.E.S. copper peaks on the calibration lines of Figure III.27 and a diffuse Pt(100)-($\sqrt{2}\times\sqrt{13}$) with intensity greatest around the Pt(100)-($\sqrt{2}\times\sqrt{2}$)R45° spot positions. The A.E.S. copper peaks were found to have increased by 11% after leaving for 5 hours and the LEED pattern was found to have changed to a Pt(100)-($\sqrt{2}\times\sqrt{2}$)R45°.

Films of 8.5 M-L and 4.5 M-L were also found to give anomalously high A.E.S. copper signals; both were associated with oxygen and sulphur impurities.

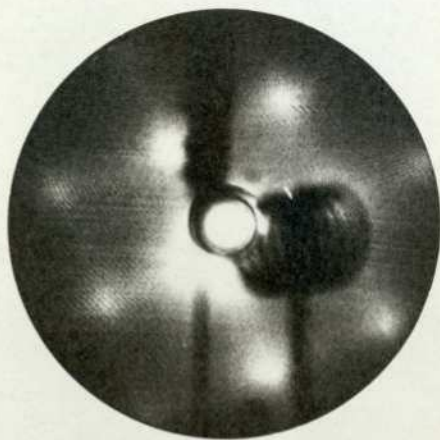
III.5.2.5 Evaporation of Copper onto Pt(100) in Oxygen

An evaporation of copper was made from the can source onto the crystal at a rate of 1 Cu(100) M-L/min. to a total of 3.2 Cu(100) M-L in an oxygen pressure of 1×10^{-7} torr. The LEED from the resulting surface, shown in Figure III.30a,



a) 48 V
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-Cu
9 M-L of Copper deposited on Pt(100) at 450°C

b) 55 V
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-Cu
9 M-L of Copper deposited on Pt(100) at 450°C



c) 34 V
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-Cu
Oxygen on 9.3 M-L of Copper on Pt(100).

d) 29 V
Pt(100) (2x2)-Cu

FIGURE III.29



a) 60 V



b) 45 V

3 M-L Copper films evaporated onto Pt(100) in Oxygen at :-
 1×10^{-7} torr 1×10^{-6} torr



c) 60 V



d) 81 V

LEED patterns after annealing crystal at :-
 300°C 700°C

FIGURE III.30

was a diffuse pattern based on a $\text{Pt}(100)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$. When annealed at 300°C for 2 periods of $\frac{1}{2}$ hour while A.E.S. was carried out separated by 4 hours in vacuum at 20°C the structure changed to a clear $\text{Pt}(100)-(2\times 2)$ while the A.E.S. showed a small sulphur peak.

Deposition of a similar thickness film on a cleaned $\text{Pt}(100)$ surface at a pressure of 1×10^{-6} torr gave a similar pattern, Figure III.30b, with diffuse intensity around the fractional order spots of a $\text{Pt}(100)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$. Again, this pattern reverted to a true $\text{Pt}(100)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ (Figure III.30c) on annealing at 300°C for 30 mins. while obtaining an A.E.S. spectrum. Further annealing to 700°C for 1 min. gave a $\text{Pt}(100)-(2\times 2)$. (Figure III.30d)

III.5.2.6 The Effect of Copper Film Thickness on A.E.S. Spectra Shape

A possible explanation of the variable A.E.S. peak sizes observed from copper overlayer films of 3-12 M-L on $\text{Pt}(100)$ was a variation in the fine structure of the copper Auger spectrum with the presence of impurities. The changes in this structure could not be detected in the normal low resolution mode ($\sim 2\frac{1}{2}\%$ resolution) but by using the higher resolution method (3 V resolution = $.33\%$ at 916 eV) some detail could be observed. In Figure III.31 the high resolution spectra of copper deposited in $\uparrow$ creasingly thick layers on $\text{Pt}(100)$ are recorded under identical operating conditions. The copper coverages were determined by running the low resolution spectra of the same surfaces and using the calibration curve of Figure III.27. A G.E.C. quartz crystal

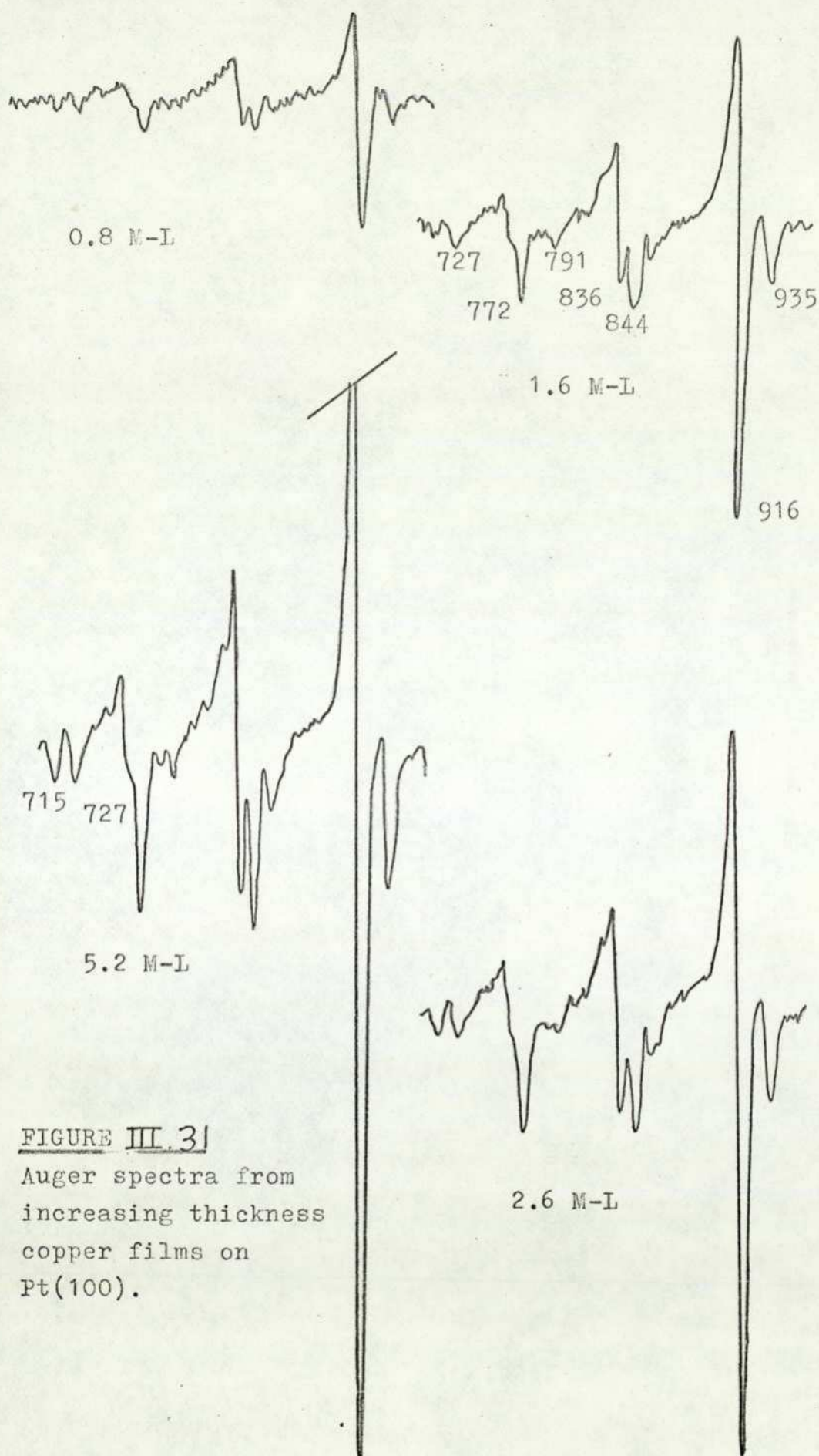


FIGURE III.31

Auger spectra from
increasing thickness
copper films on
Pt(100).

was used to monitor the rate of deposition.

III.5.2.7 Effect of Impurities on A.E.S. Spectra Shape

The high resolution mode of A.E.S. was used to determine if the presence of impurities in the copper overlayer film affected the copper peak shapes. In Figure III.32 the spectrum from a sulphur covered copper overlayer exhibiting a Pt(100)-(2x2)-Cu/S may be compared with that from a clean copper overlayer surface exhibiting a Pt(100)-(1x1)-Cu.

A similar comparison to the clean copper overlayer surface was made with copper films evaporated in a high pressure of oxygen so that a large oxygen peak was also observed.

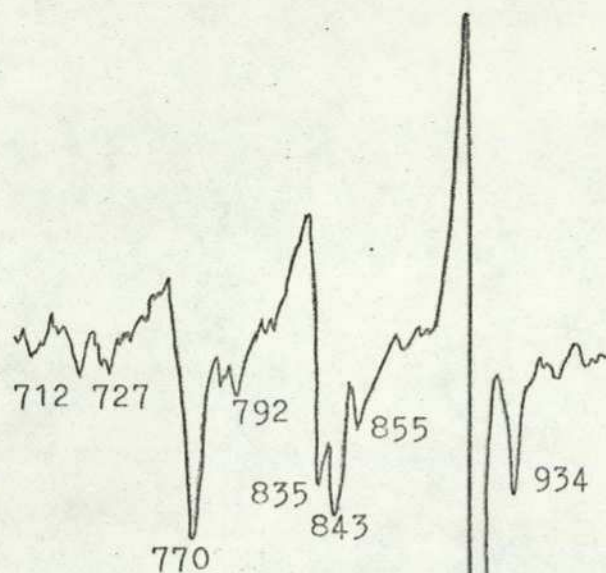
No significant changes in peak shapes or relative sizes were observed between these cases or peak position shifts beyond the intrinsic error of repeatability of ± 1 eV.

III.5.3 The Evaporation of Gold onto Pt(100)

A short series of experiments was carried out on the properties of a thin gold overlayer on platinum. Both metals exhibit the anomalous (100)-(5x1) type pattern on their (100) faces. Although the patterns are not identical it is probable that they are caused by a similar effect in each metal.

III.5.3.1 Experimental Procedure

The gold was evaporated from a tungsten wire 'hairpin' source at a rate of ~ 1 Au(100) M-L/min and monitored with a G.E.C. 9.43055 MHz crystal in the forward direction i.e. 10° from the source-crystal direction. The wire was screened so that evaporation to the crystal occurred only from



b) Sulphur covered Copper on Pt(100)
LEED shows Pt(100) (2x2)-Cu/S

915

a) Clean Copper on Pt(100)
LEED shows Pt(100) (1x1)-Cu

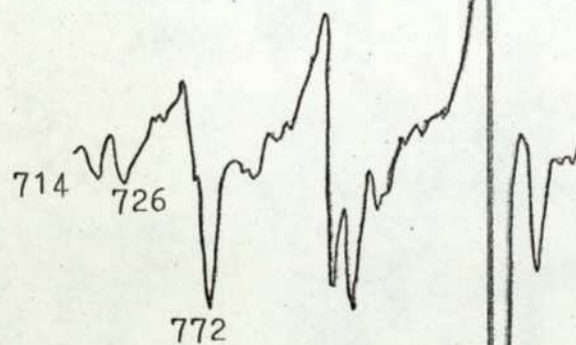


FIGURE III.32

Auger Spectra from similar thickness
(2.5 M-L) Copper films on Pt(100)

the bottom 1.5 mm at the tip of the 'hairpin'. The calibration was taken to be that obtained for copper with a correction for difference in mass:

$$\text{Gold deposition flux} = \frac{\text{Copper Calibrated Flux} \times \text{Copper Density}}{\text{Gold Density}}$$

Evaporation was arranged so that the crystal could be partially shielded behind the R-F coil to enable easier comparisons between the LEED patterns from a clean Pt(100) and various gold overlayers to be made. The pressure did not exceed 2×10^{-9} torr during evaporation, with carbon monoxide as the major gas component.

A.E.S. spectra were obtained with a 3 V resolution by operating the spectrometer so that the grids only detected 130 eV electrons while the range of possible energies above this value was scanned with a varying positive potential on the crystal.

III.5.3.2 Results - Gold on Pt(100)

a) 0.28 Au(100) M-L. The LEED pattern showed a sharp Pt(100) $-(1 \times 1)$ with diffuse Pt(100) $-(\sqrt{2} \times \sqrt{2})R45^\circ$. The uncovered part of the crystal retained the cleaned surface Pt(100) $-(5 \times 1)$ pattern. The two A.E.S. spectra taken under identical conditions with only a small vertical shift of the crystal to transfer from the clean to the covered surface showed no change in peak positions but the peaks from the gold covered area were 10-20% lower.

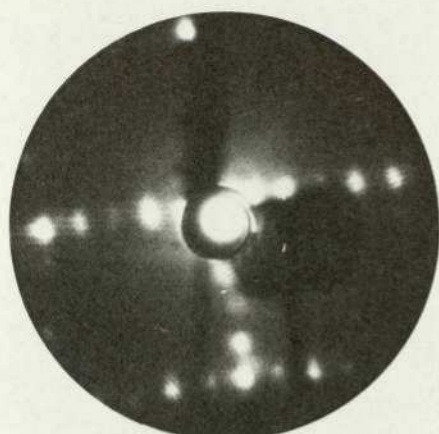
b) 0.76 Au(100) M-L. With additional gold added to bring the total coverage to 0.76 M-L at the Au(100) spacing, the

LEED pattern was found to be a more diffuse Pt(100)-(1x1) with weak Pt(100)-($\sqrt{2}\times\sqrt{2}$)R45°. Figure III.33a-d shows the clean surface LEED pattern, the pattern with the incident beam at the boundary of the overlayer, and the patterns from the gold covered surface at two beam energies. The A.E.S. spectrum of the gold covered area showed slight upward shifts of the positions of several of the platinum peaks as the gold signal appeared.

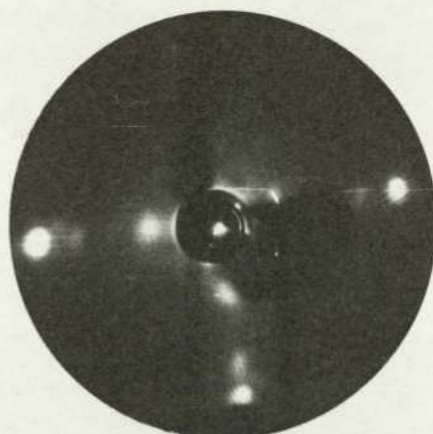
c) 1.8 Au(100) M-L. Gold was added to give a total of 1.8 M-L. The LEED pattern was then a Pt(100)-(1x1) and is shown in Figure III.33e,f. The change in surface mesh associated with the surface taking the gold spacing could not be detected as the shift would be similar to the spot size. The A.E.S. spectra on and off the overlayer were dissimilar particularly in the range 140-180 eV. The peaks recorded from the gold 1.8 monolayer cover at 392 and 356 eV were ~50% of those of similar energy from the clean platinum.

The crystal was cleaned and a series of heavier evaporations carried out.

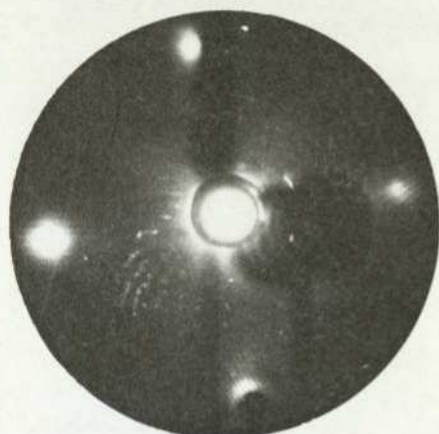
A single evaporation of 1.7 Au(100) M-L again gave a surface with a (1x1) LEED pattern adjacent to the cleaned surface Pt(100)-(5x1). After an evaporation to 4.7 Au(100) M-L the LEED pattern from the gold surface was found to have developed an Au(100)-(nx1) pattern similar to Pt(100)-(5x1). This pattern is shown in Figure III.34a,b,d; III.34c shows the Pt(100)-(5x1) remaining on the uncovered part of the crystal. The clarity of the spots increased slightly (Figure III.34e) after an A.E.S. spectrum had been taken of



a) 57 V



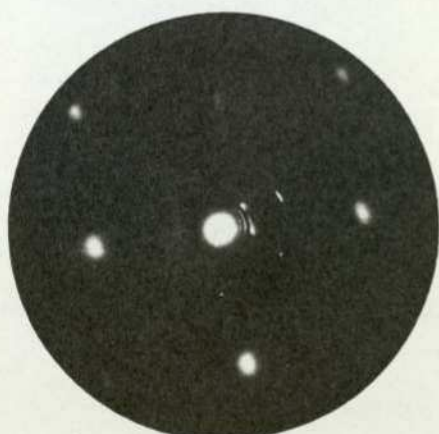
b) 57 V



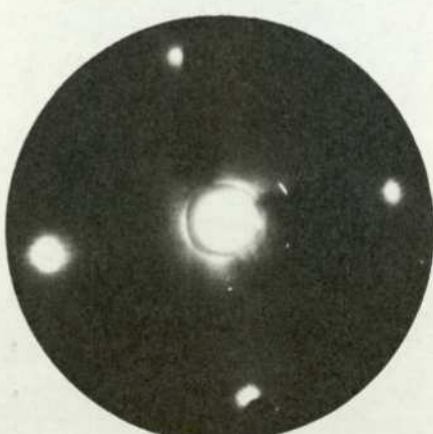
c) 60 V



d) 39 V

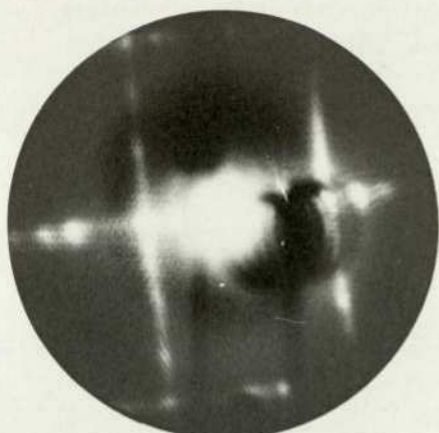


e) 98 V

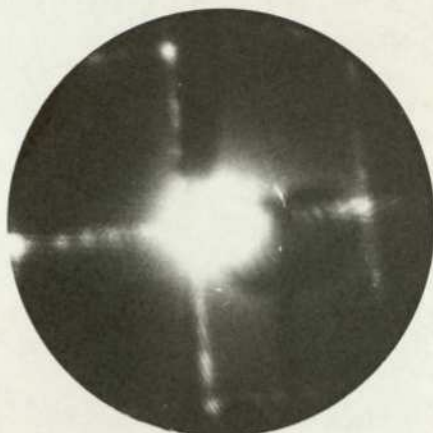


f) 60 V

FIGURE III.33 LEED patterns from Pt(100) with Gold overlayer
a) Cleaned Pt(100). b) LEED beam at edge of Gold film.
c,d) Gold film 0.76 M-L. e,f) Gold film 1.8 M-L.



a) 52 V



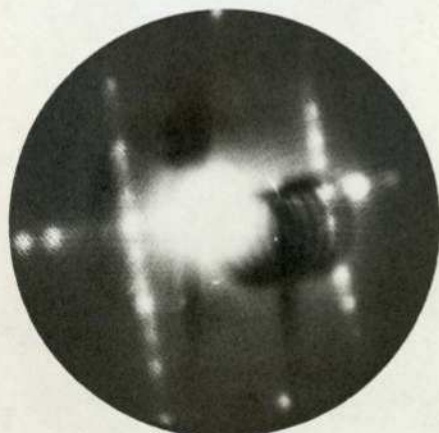
b) 55 V



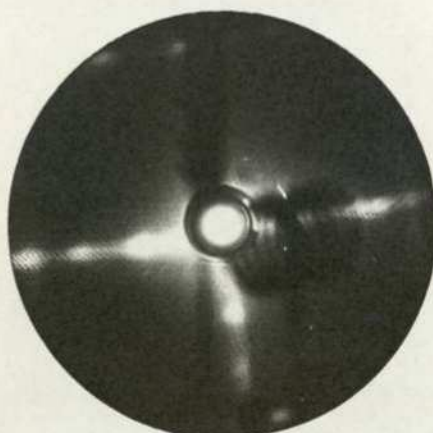
c) 51 V



d) 51 V



e) 46 V



f) 50 V

FIGURE III.34 LEED patterns from Gold on Pt(100).

c) Pt(100) (5x1) cleaned surface.

a,b,d) A 4.7 M-L film of Gold on Pt(100).

e) After annealing at 300°C f) 6.2 M-L of Gold on Pt(100).

the surface which caused the crystal to be annealed for 30 mins. The spots were indexed as an Au(100)-(7x1).

Evaporation of gold to a 6.2 Au(100) M-L film gave an Au(100)-(nx1) based on an Au(100)-(7x1) with high intensity at (0,3/7), (0,5/7), (0,1) positions. This pattern is shown in Figure III.34f and III.35a.

On annealing this crystal at 450°C for 5 mins. the pattern was found to have changed to the lower coverage $\sim$ (7x1) pattern, Figure III.35b.

After annealing at 530°C for 5 mins. the pattern modified further as shown in Figure III.35c. This remained at 610°C; Figures III.36 a and b compare the gold and platinum surfaces.

After annealing at 700°C the pattern reverted to (1x1) but showed diffuse intensity around the $(\frac{1}{2}, \frac{1}{2})$ positions at low beam voltages - Figure III.35d. The Pt(100)-(1x1) was observed up to 900°C (Figure III.36c,d).

The surface pattern reverted to a Pt(100)-(5x1) on both areas of the crystal after annealing the crystal at 1000°C for 10 mins.

The A.E.S. spectra of the clean surface, +1.7 M-L and +4.7 M-L are shown in Figure III.37.

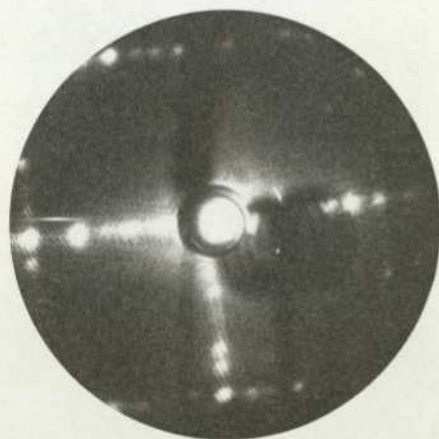
For these thin gold films measured at a low resolution the appearance of new A.E.S. peaks adjacent to the platinum peaks was not clearly resolved. The heights of most platinum peaks dropped as the gold peaks increased with increasing thickness of the gold film. Figure III.37 was obtained using the higher resolution biased crystal method to show the similar shape of the gold spectrum to that of platinum.



a) 50 V
6.2 M-L of Gold on Pt(100)



b) 50 V
After anneal at 450°C

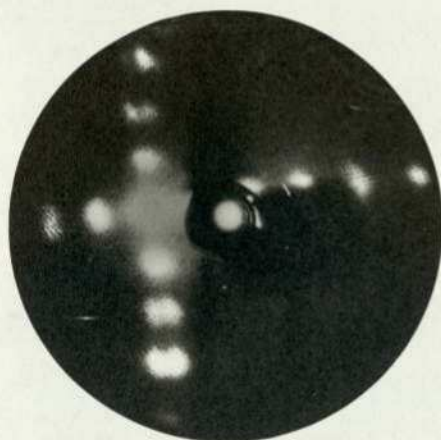


c) 56 V
After anneal at 530°C



d) 37 V
After anneal at 700°C

FIGURE III.35 LEED patterns from Gold on Pt(100).
Effects of annealing a 6.2M-L film.

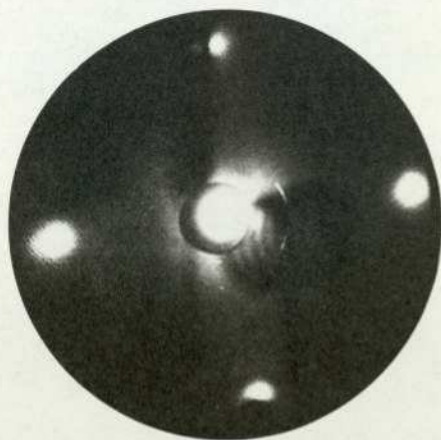


a) 27 V
Cleaned Pt(100)
Upper half of crystal
Pt(100) (5x1)

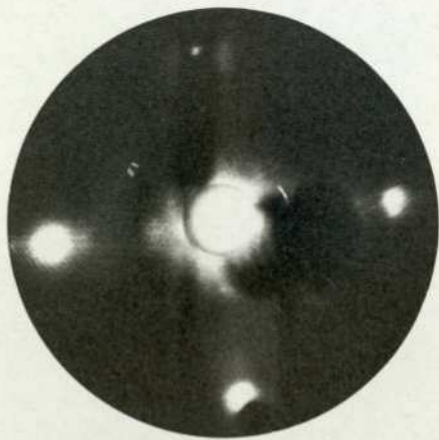


b) 27 V
Gold covered Pt(100)
Lower half of crystal
Pt(100) (7x1)-Au

Annealed at 610°C



c) 57 V
After anneal at 800°C

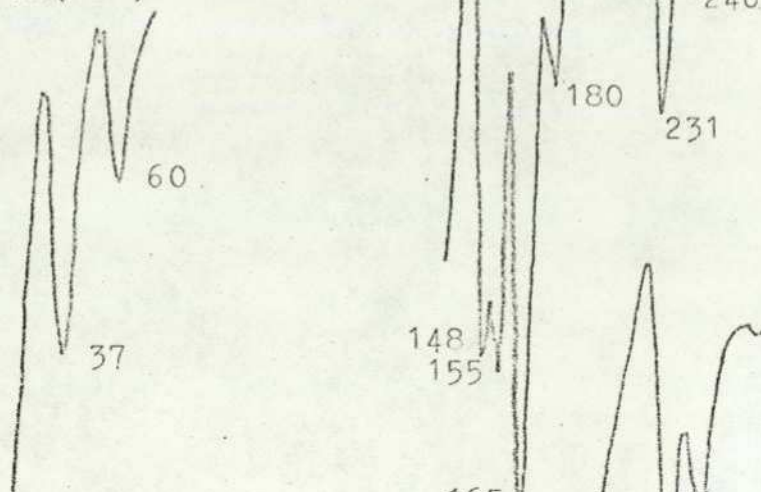


d) 58 V
After anneal at 900°C

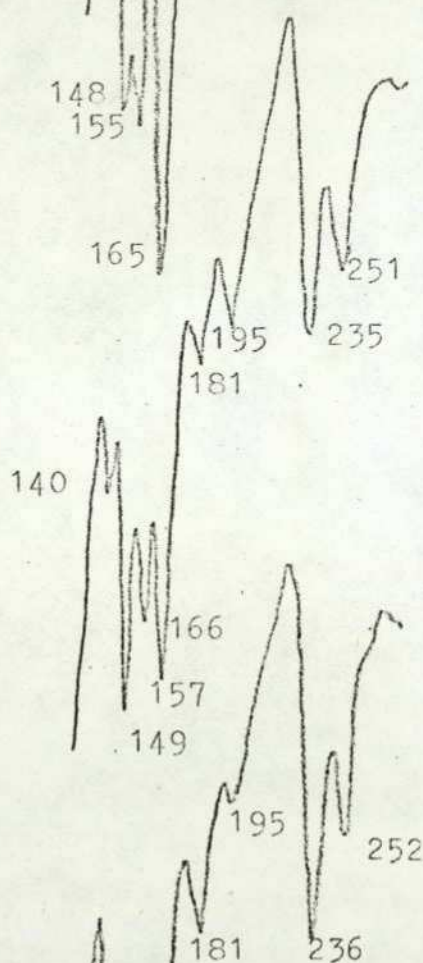
FIGURE III.36 LEED patterns from Gold on Pt(100).
Further annealing of a 6.2 M-L film.

Auger Spectra showing Au peaks
replacing those from the Pt(100) substrate.

a) Clean Pt(100)



b) 1.7 M-L film of Au.



c) 4.7 M-L film of Au.

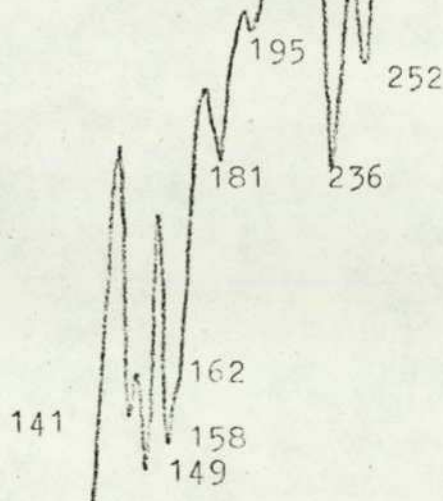


FIGURE III.37

III.6 The Absorption of Simple Gases on Surfaces of Films

The structures determined for the growth of copper or gold on the platinum indicated that the geometries of the films were characteristic neither of substrate nor the film material in its bulk arrangement. This condition is normal in most alloy systems where the admixture of components at the surface is variable over extensive limits. In this system of controlled deposition the changes in adsorption structures and compositions were tested with simple gases.

III.6.1 Addition of Oxygen

III.6.1.1 Cleaned Pt(100)

Although large oxygen A.E.S. peaks had been observed from the crystal after cleaning treatments of $>2 \times 10^{-7}$ torr in oxygen at 1000°C , no oxygen peaks developed during less severe exposures. The Pt(100)-(5x1) pattern was unchanged by an exposure of 1000 L on the room temperature crystal at a gas pressure of 5×10^{-7} torr. The A.E.S. spectrum was unchanged from the cleaned surface pattern but was not directly comparable as the electron beam raised the crystal temperature to 300°C . However, when the spectrometer was pre-set to scan the oxygen peak within 20 s of moving the electron beam onto the crystal to avoid raising the temperature above 50°C , again no oxygen was detected.

In a poor vacuum due to insufficiently outgassed system components the addition of oxygen at low pressures of $<1 \times 10^{-8}$ torr total gauge pressure resulted in very small O_2^+-32 and O^+-16 mass spectrometer peaks with largely increased

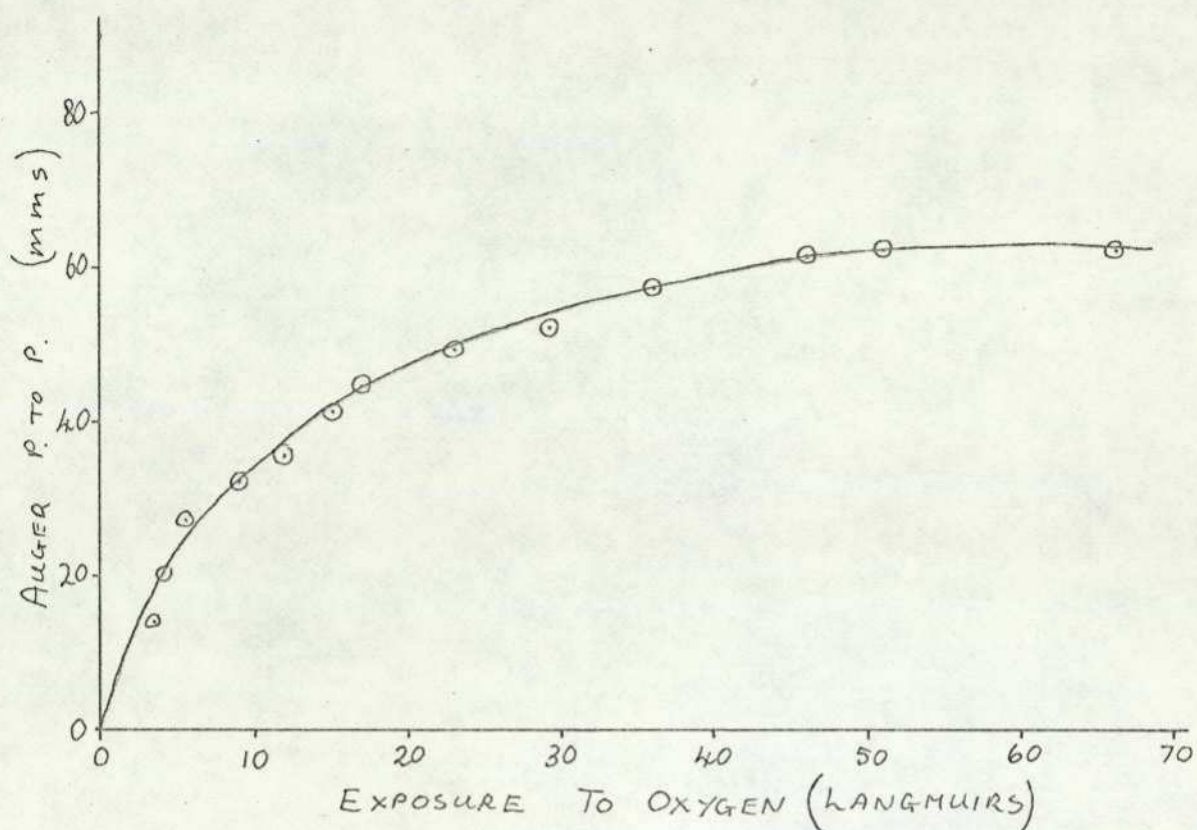
CO⁺-28. Under these conditions the Pt(100)-(5x1) patterns slowly changed to a Pt(100)-(1x1) with increased surface carbon levels indicating absorption and cracking carbon monoxide on the surface.

III.6.1.2 Oxygen on Low Coverage Copper Films on Pt(100)

Absorption of oxygen on low coverage 1 Cu(100) M-L copper films on the Pt(100) crystal substrate was monitored with A.E.S. which resulted in a crystal temperature of 300°C during absorption. The major oxygen A.E.S. peak, recorded at 6 V resolution at 518 eV, was monitored as oxygen was admitted to the system at 8×10^{-8} torr. The O₂⁺-32 mass spectrometer peak was >10 times the height of the CO⁺-28 peak. The oxygen peak size was plotted against oxygen exposure and this is shown in Figure III.38b. An A.E.S. spectrum was taken after an exposure of a similar film to oxygen whilst monitoring the LEED patterns, i.e. with the crystal within a few degrees of room temperature. The major oxygen peak was within 10% of the value obtained in the Auger beam heated case. The oxygen peak size was unaffected by exposure in the A.E.S. electron beam for 20 mins. with associated sample heating to 300°C.

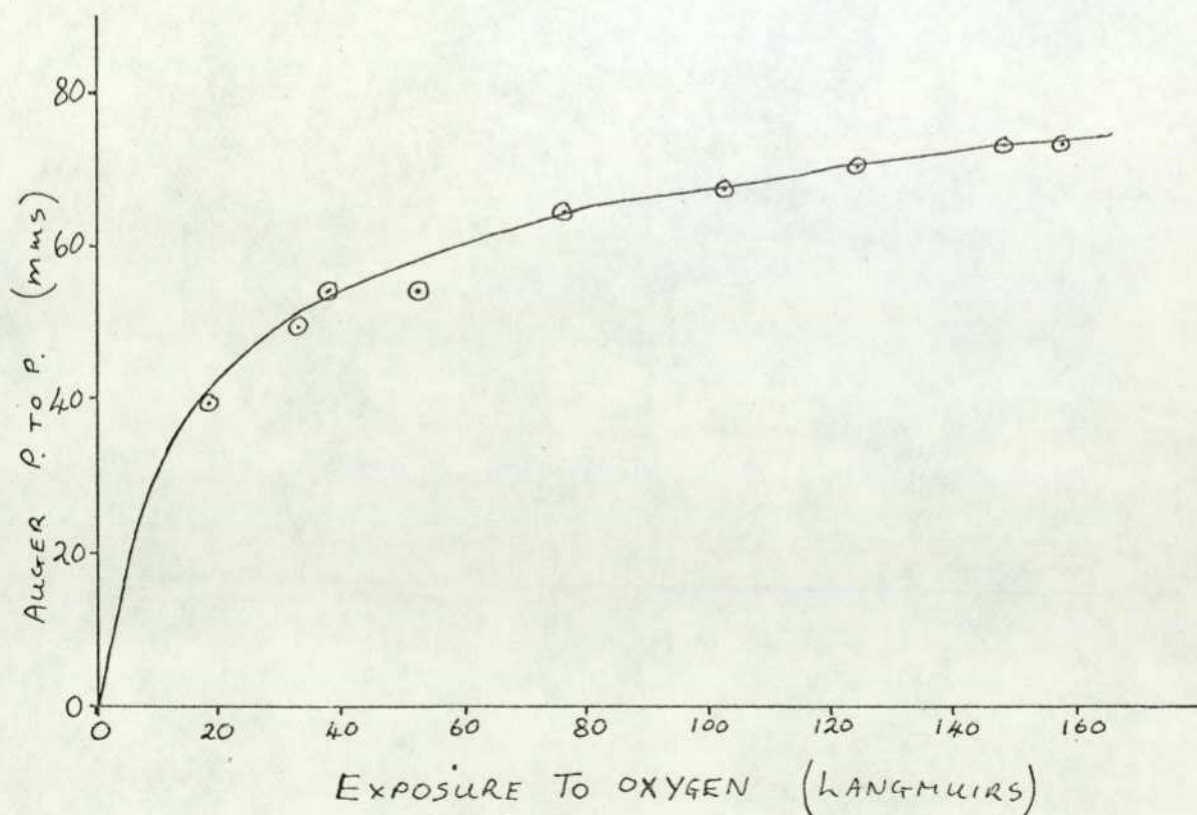
Oxygen added to the low copper film coverage crystal surfaces at 20°C caused the LEED pattern to change from the clean surface Pt(100)-(1x1)-Cu to a weak Pt(100)-($\sqrt{2} \times \sqrt{2}$)R45°.

When oxygen was added at 8×10^{-8} torr to the crystal copper overlayer surface at 300°C the surface mesh changed from the Pt(100)-(1x1)-Cu pattern, Figure III.39a, to the Pt(100)-($\sqrt{2} \times \sqrt{3}$) pattern shown in Figure III.39b. The

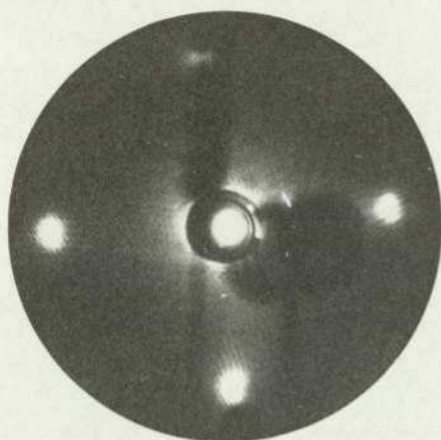


a) Oxygen on 5 Cu(100) M-L of Copper on Pt(100).

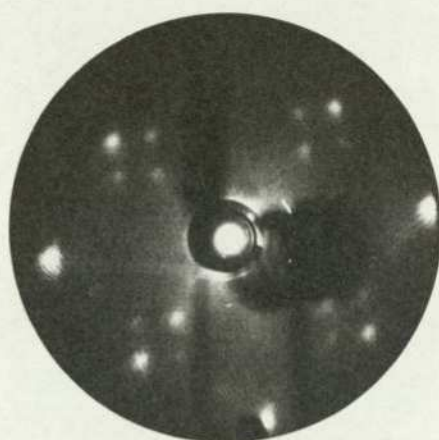
FIGURE III.38



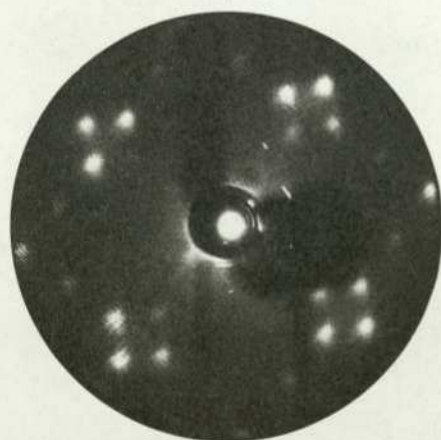
b) Oxygen on 1 Cu(100) M-L of Copper on Pt(100).



a) 60 V
Copper on Pt(100)
Pt(100) (1x1)-Cu



b) 50 V
After O₂ treatment at 300°C
Pt(100) ($\sqrt{2} \times \sqrt{3}$)-Cu/O



c) 45 V
H₂S added to surface b)



d) 32 V
After annealing at 300°C

FIGURE III.39 Oxygen on 1 M-L of Copper on Pt(100).

A.E.S. spectrum of the surface at this time showed very little sulphur.

To assist in the interpretation of this pattern the crystal was treated with H_2S at 1×10^{-9} torr total pressure (with H_2S -34 peak 50% of CO-28 peak on mass spectrometer) for 2 mins. The geometry of the pattern was unchanged but the spots around the $(\frac{1}{2}, \frac{1}{2})$ positions were strengthened - Figure III.39c.. After a total of 10 L exposure to H_2S the crystal was again annealed to 300°C when the pattern was found to have changed to the $\text{Pt}(100)-(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ (Figure III.39d). These patterns are of relevance to the explanation of the patterns observed after copper was evaporated in oxygen.

III.6.1.3 Oxygen Adsorption on Higher Coverage Copper on Pt(100).

Oxygen was again added at 8×10^{-8} torr to a heavier deposition of copper ($\sim 8 \text{ Cu}(100) \text{ M-L}$) on the $\text{Pt}(100)$ crystal. The increase in the oxygen A.E.S. peak size with exposure is plotted in Figure III.38a. This corresponded to absorption at 300°C due to the effect of the A.E.S. electron beam. The initial diffuse LEED $(100)-(1 \times 1)$ pattern changed to a sharper $(100)-(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ during a total exposure of 70 L of oxygen.

A $9 \text{ Cu}(100) \text{ M-L}$ film of copper on $\text{Pt}(100)$ was exposed to oxygen to a total of 70 L at 20°C when the A.E.S. oxygen peak was $\sim 15\%$ lower than that found for the earlier case. The film was contaminated with sulphur as indicated by a small 150 eV peak in the A.E.S. spectrum and the LEED pattern

observed after the oxygen addition was a (100)-(2x2). (Figure III.29c,d).

III.6.2 Addition of Hydrogen Sulphide

The interaction of H_2S with metal surfaces was found to be very rapid, requiring a low exposure rate to enable the surface adsorption to be monitored by LEED and A.E.S. It was necessary to flush the gas dosing system with H_2S several times to reduce the contamination of the added gas by other gases desorbed from the pipe-work. When the gas from the dosing line was admitted to the main chamber the increase in pressure recorded on the ionisation gauge did not correspond to the H_2S^+-34 peak on the mass spectrometer. From a residual pressure of 4×10^{-10} torr addition of H_2S at a total pressure of 1×10^{-9} torr increased the CO^+-28 peak by 50% and the H_2S^+-34 peak to 70% of the increased CO peak. Water and carbon dioxide peaks were also increased by desorption from the system walls. Under the conditions used for monitored growth of the surface sulphur concentration, i.e. $0.5-1.5 \times 10^{-8}$ torr total pressure, the H_2S^+-34 mass spectrometer peak was at least twice the CO^+-28 peak. The other major peak H_2^+-2 was due to both desorption from the system surfaces and cracking of the H_2S . At constant recorded total pressure the H_2S^+-34 peak increased with time at the expense of the others.

III.6.2.1 A.E.S. of H_2S on Pt(100) and Surface Copper

Due to the rapid adsorption of the sulphur, adsorption characteristics were plotted against exposures calculated from ion gauge total pressure readings. The true nitrogen

equivalent exposures to H_2S should be $\frac{2}{3}$ of those plotted. For comparison, the exposures of the clean Pt(100) crystal and the single monolayer of copper on Pt(100) were made under these conditions (Figure III.40,41). The effect of adding H_2S at too low a pressure so that the partial pressure rose only slowly, was observed as an adsorption characteristic as in Figure III.42.

The three cases shown all represent adsorption of H_2S on a sample maintained at 300°C by the Auger electron beam. No variation of the sulphur signal from the surface was observed when the beam position on the crystal was changed slightly, indicating a lack of beam cracking or desorption. The sulphur peak size at the end of a series of exposures to H_2S was stable with the sample in the beam for at least 1 hour after the final exposure. Changes of $<10\%$ were attributed to variation in total beam current after the filament poisoning by H_2S altered the emission characteristics of the electron gun.

III.6.2.2 LEED of H_2S on Pt(100) and Surface Copper

The LEED results for H_2S adsorption on clean Pt(100) followed reported surface structures^(62,63). With the cleaned crystal at 20°C , H_2S rapidly caused the Pt(100)-(5x1) pattern to disappear after an exposure of <1 L and a Pt(100)-(1x1) to form. With increasing exposure this changed to a strong Pt(100)- $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ which was stable in vacuum for many days (Figure III.43d).

H_2S adsorption on the copper surface film on Pt(100) in the range 0.5 to 3.0 Cu(100) M-L consistently caused a

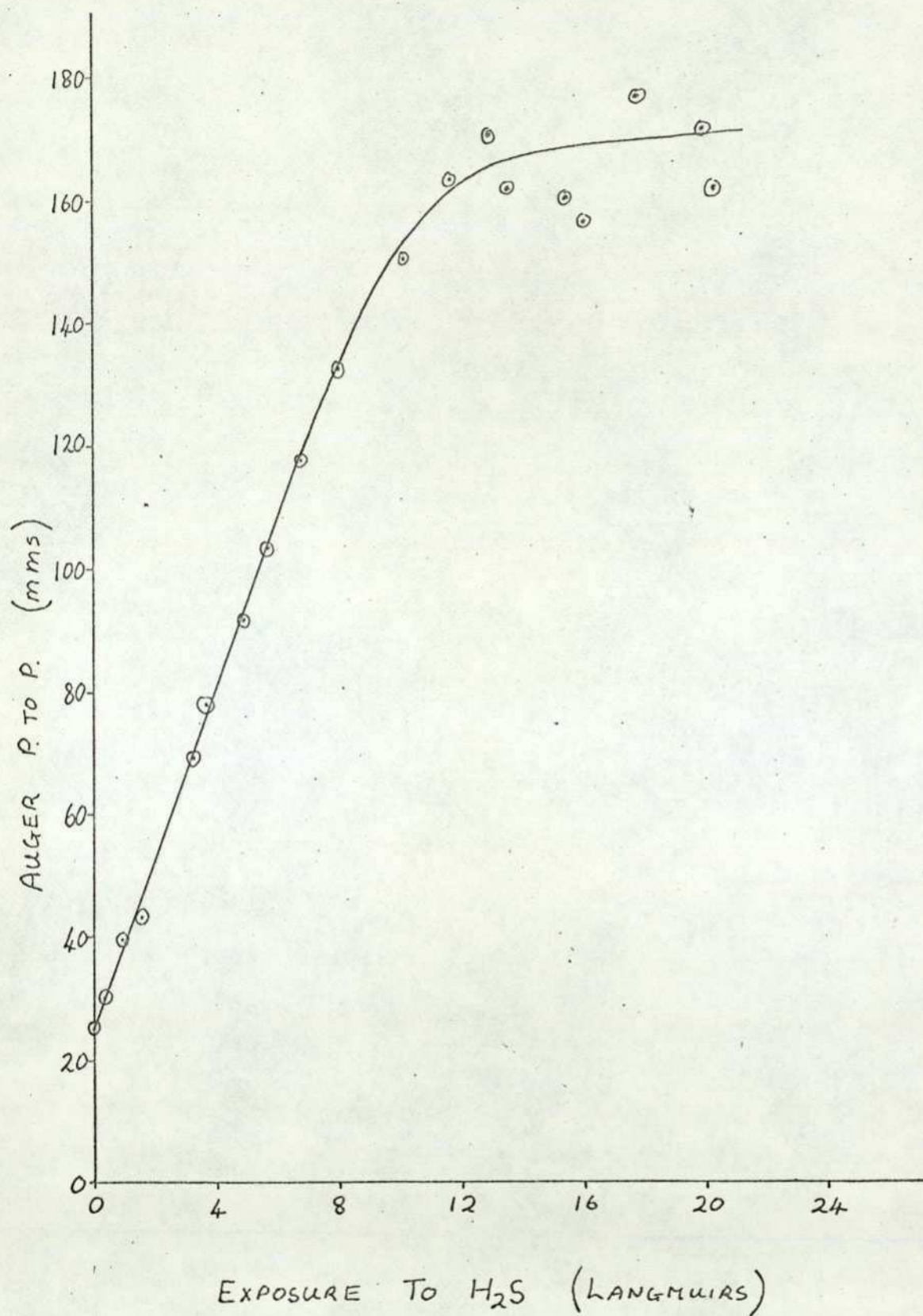


FIGURE III.40 Adsorption of H₂S on cleaned Pt(100) at 300°C

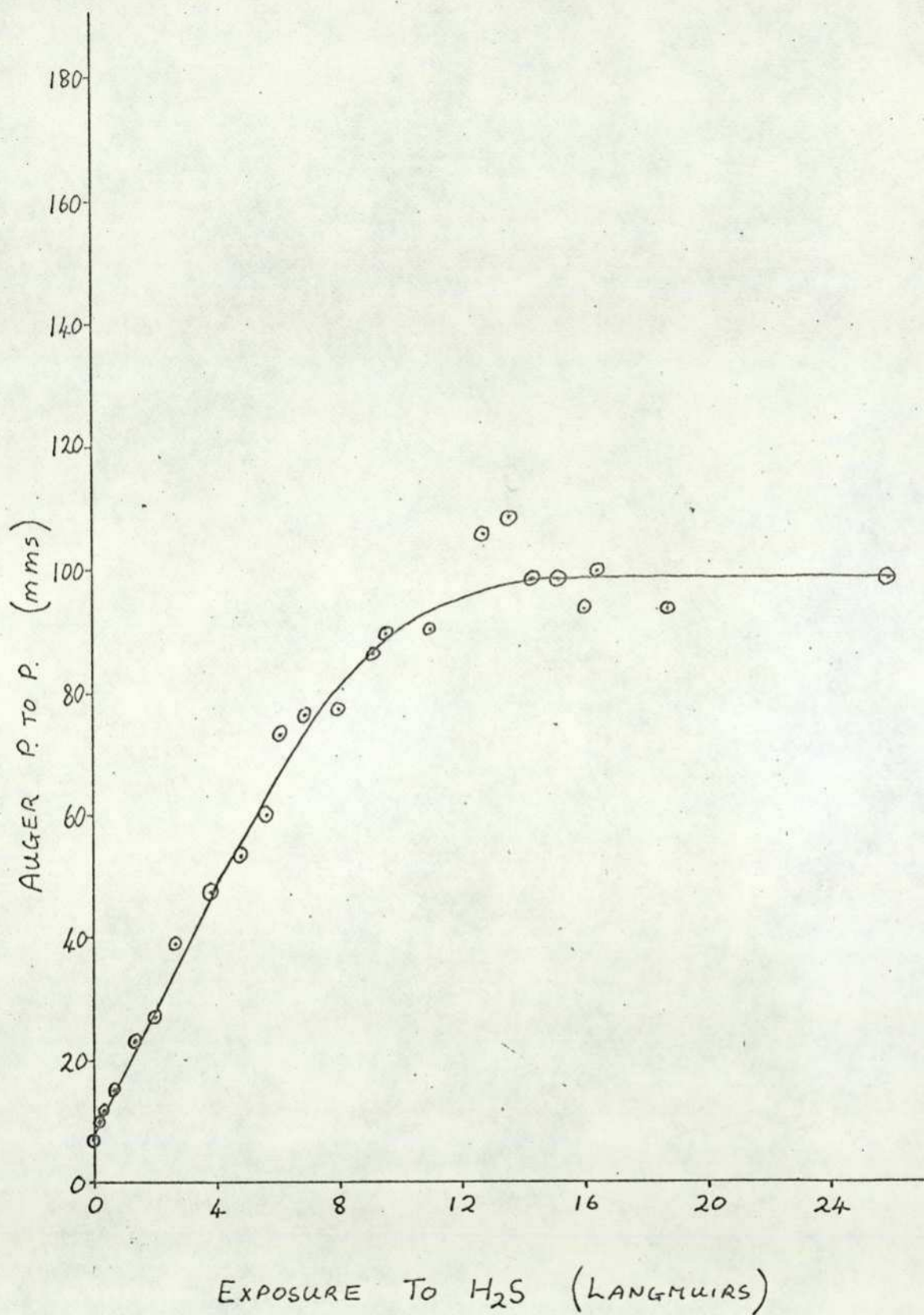
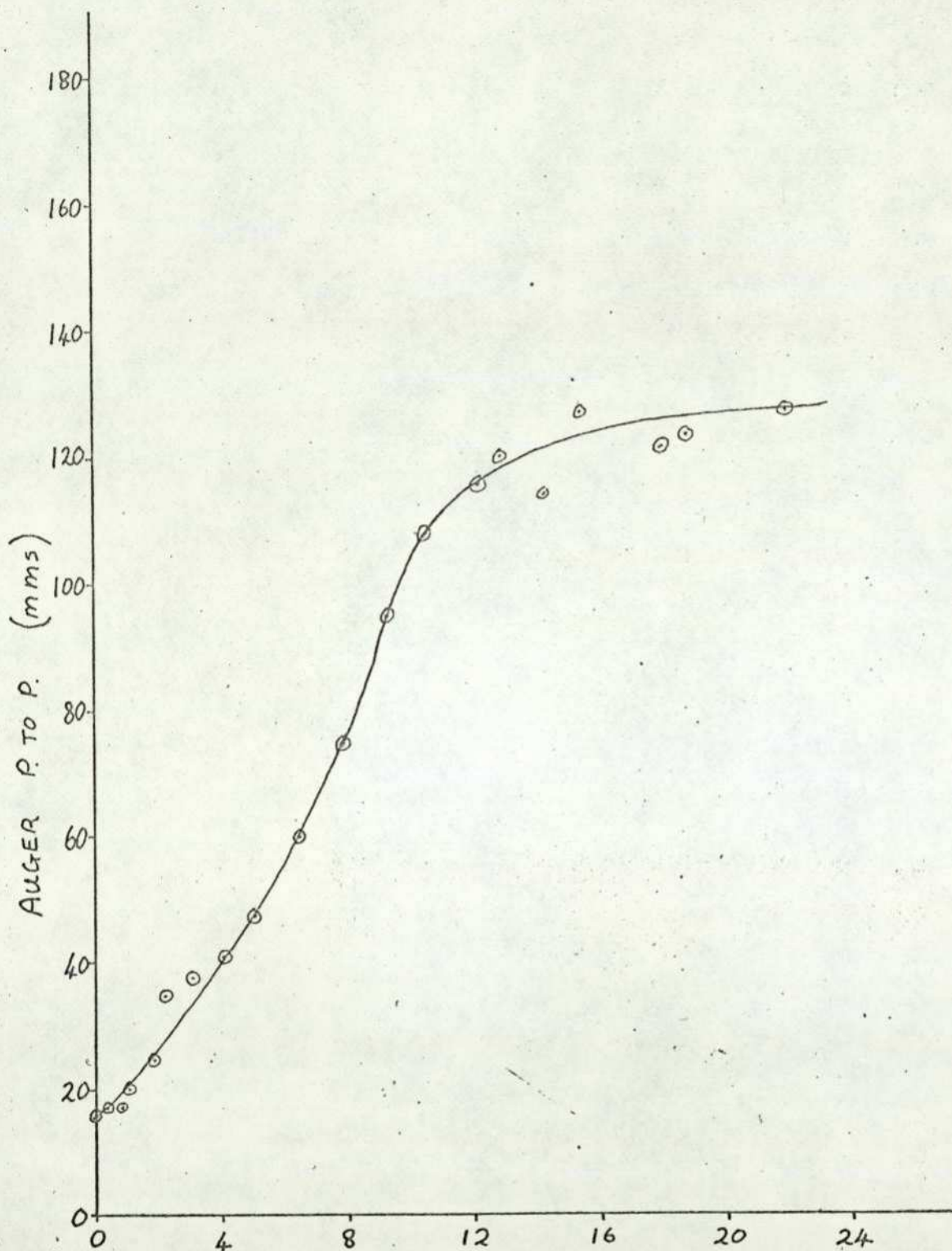


FIGURE III.41 Adsorption of H₂S on 1.2 M-L of Copper on Pt(100)



EXPOSURE TO H₂S (LANGMUIRS)

FIGURE III.42 Adsorption of H₂S on 0.5 M-L of Copper on Pt(100)
The exposure axis is distorted due to varying H₂S partial pressure.

Pt(100)-(2x2)-Cu/S to form. On the surface at 20°C the pattern was weak and not sharply defined. However, the annealing effect of the A.E.S. electron beam caused a sharpening of this pattern. The (2x2) pattern formed after an exposure of <4 L of H₂S and remained with exposure of 200 L. Examples of this pattern are shown:-

Figure III.43a This is the Pt(100)-(2x2)-Cu/S on 2 M-L of copper, after 15 L of H₂S at 300°C.

Figure III.43b H₂S formed Pt(100)-(2x2)-Cu/S on 1 M-L of copper, after 25 L of H₂S.

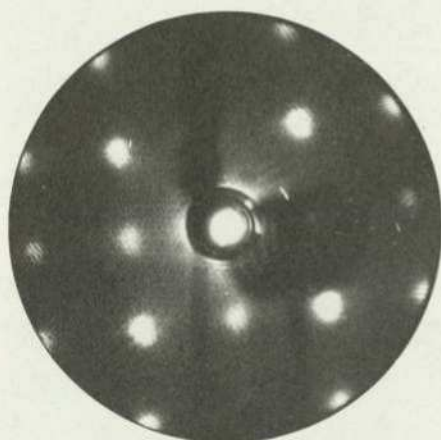
Figure III.43c H₂S formed Pt(100)-(2x2)-Cu/S on 0.5 M-L of copper, after 20 L of H₂S.

These patterns were clearly (2x2) meshes but the spots of the $(\sqrt{2} \times \sqrt{2})R45^\circ$ pattern were stronger than the remaining spots.

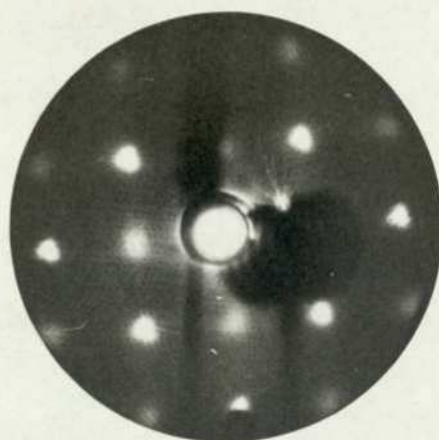
III.6.2.3 H₂S on a Gold Surface on Pt(100)

The LEED patterns resulting from the adsorption of H₂S gas on the cleaned Pt(100) surface could be compared with that on the Pt(100) surface with 1.8 Au(100) M-L coverage by a small vertical movement of the crystal manipulator to bring the appropriate part of the crystal into the electron beam.

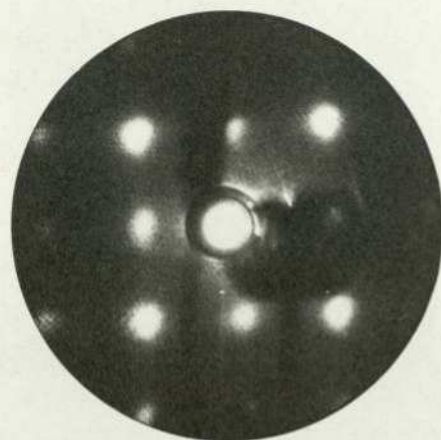
After an exposure of 2 L at a total pressure of 1×10^{-8} torr the clean Pt(100) surface showed a strong Pt(100)- $(\sqrt{2} \times \sqrt{2})R45^\circ$ while the gold covered surface developed the same pattern but much weaker.(Figure III.44a). The patterns were unchanged by a further 10 L of H₂S. When left overnight the patterns were unchanged and are shown in Figure III.44b,d. Comparison of the negatives of this pair of photographs



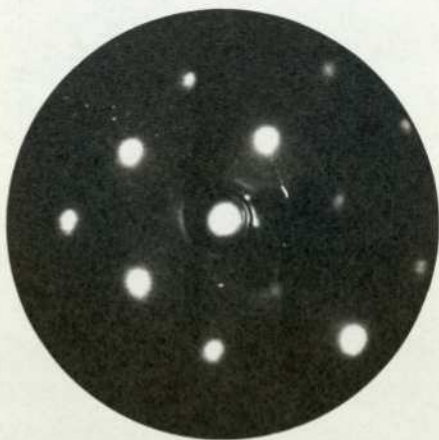
a) 50 V
2.0 M-L of Copper
Pt(100) (2x2)-Cu/S



b) 60 V
1.0 M-L of Copper
Pt(100) (2x2)-Cu/S

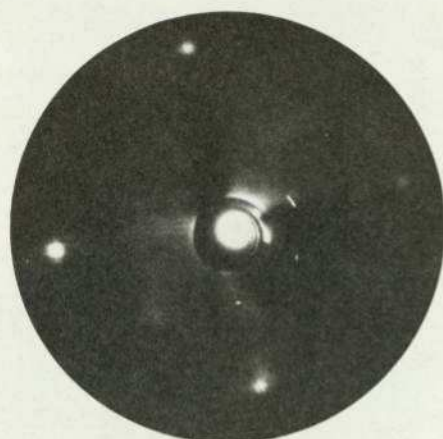


c) 50 V
0.5 M-L of Copper
Pt(100) (2x2)-Cu/S



d) 90 V
No Copper
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-S

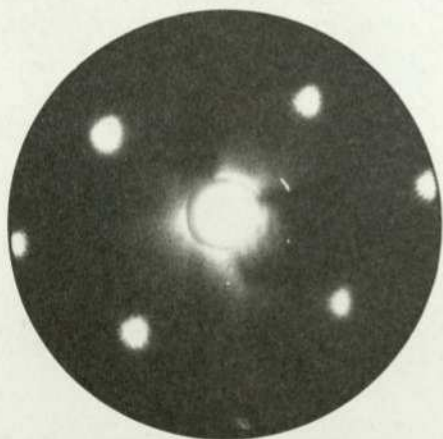
FIGURE III.43 LEED patterns from H₂S adsorption on cleaned and Copper covered Pt(100).



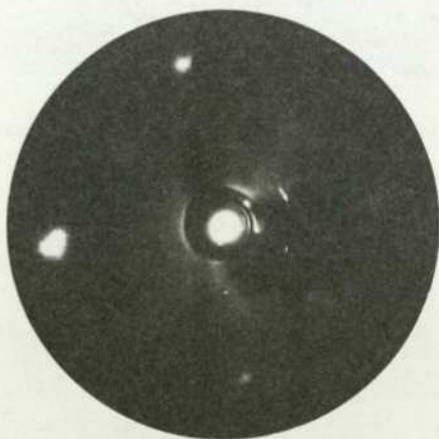
a) 60 V
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-Au/S
Gold on Pt(100)



b) 66 V
Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45°-S
Cleaned Pt(100)



c) 44 V
After annealing Au/S film(a)
at 300°C



d) 68 V
Gold on Pt(100)

FIGURE III.44 LEED patterns showing variation of the strength of Pt(100) ($\sqrt{2} \times \sqrt{2}$)R45° from H₂S treatment of cleaned and Gold covered (1.8 M-L) Pt(100).

indicated a small expansion of $\sim 3\%$ in the gold covered surface (1x1) mesh compared with the uncovered (1x1) mesh. After taking an A.E.S. spectrum which annealed the crystal to 300°C for 30 mins. the gold covered surface was found to exhibit a strong $(\sqrt{2}\times\sqrt{2})R45^{\circ}\text{-Au/S}$ pattern, Figure III.44c, identical to that on the uncovered surface. The 150 eV A.E.S. peak of sulphur on the gold surface was 36% of that on the platinum surface.

III.6.3 Adsorption of Carbon Monoxide

Adsorption of carbon monoxide detected by the LEED and A.E.S. was considerably modified by the incident electron beam. The effects of the beams were not investigated. As has been reported for other surfaces the adsorption of carbon monoxide was not accompanied by growth of both the carbon and oxygen A.E.S. peaks.

The results obtained for adsorption on the cleaned Pt(100) crystal and on the copper overlayers were not quantitatively repeatable. However the following qualitative results were obtained.

III.6.3.1 Cleaned Pt(100)

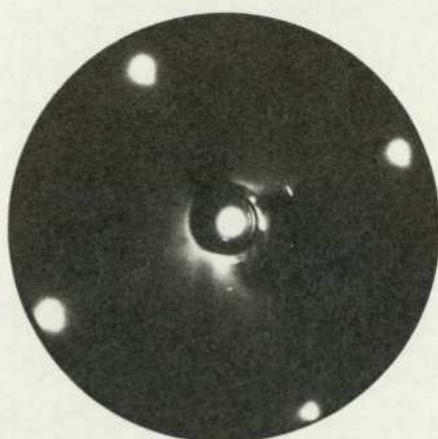
With exposure to CO of up to 1000 L the carbon A.E.S. signal increased while no oxygen signal was detected above noise. The rate of carbon signal increase was greatest under the A.E.S. electron beam irradiation. The clean surface Pt(100)-(5x1) was changed to a Pt(100)-(1x1).

III.6.3.2 1.5 M-L Copper on Pt(100)

In this case the oxygen A.E.S. peak rose during a 400 L exposure on the crystal in the electron beam, while the



a) 43 V
Pt(100) (2x2)-Cu/CO
Adsorption at 20°C



b) 50 V
Pt(100) (2x2)-Cu/CO
Adsorption at 300°C

1.5 M-L of Copper on Pt(100)



c) 122 V
Diffuse pattern, as deposited



d) 50 V
After annealing at 400°C

5 M-L of Copper on Pt(100)

FIGURE III.45 LEED patterns from Carbon Monoxide adsorption on Copper covered Pt(100).

carbon signal was little changed from its initial low value. The pressure for both the clean surface exposure and copper surface exposure was $6 - 10 \times 10^{-8}$ torr. Further exposure on this surface at 20°C with heating effects of the electron beam minimised by short irradiation caused a further small increase in oxygen level. The LEED patterns exhibited from CO treated copper covered surface are shown in Figure III.45a - a clear $\text{Pt}(100)-(2 \times 2)$ on a 20°C surface and Figure III.45b - a weak $\text{Pt}(100)-(2 \times 2)$ at 300°C .

III.6.3.3 2 M-L of Copper on Pt(100)

This surface gave an increasing oxygen A.E.S. signal with increasing exposure to carbon monoxide but with no build up of carbon. The oxygen level reached in this case was 25% of that in the 1.5 M-L case at the same exposure (600 L).

III.6.3.4 Heavy Copper Film on Pt(100)-(>5 M-L)

Exposure to 600 L of carbon monoxide at both 20°C and 300°C gave no increase in carbon or oxygen A.E.S. levels. The LEED pattern remained complex and diffuse Figure III.45c. This pattern changed to the $\text{Pt}(100)-(\sqrt{2} \times \sqrt{2})\text{R}45^{\circ}$ after annealing at 400°C for 20 mins. (Figure III.45d).

CHAPTER IV DISCUSSIONS

IV.1 The Pt(100)-(5x1). Clean Surface Structure?

The current literature on the controversy over the cause of this anomalous surface structure is described in the introduction (section I.3.1). Further experimental results are presented above. The following points are important.

- 1) The (5x1) patterns appear after surface smoothing by annealing. Any treatment which causes roughening on an atomic scale causes the (100)-(1x1) pattern to form. Such roughening may be due to argon ion bombardment, gas adsorption or metal deposition.
- 2) The (5x1) pattern may exist when no impurities are detected by A.E.S.
- 3) The (5x1) pattern may co-exist with other, impurity, patterns but these may be only from patches within the LEED beam.
- 4) For gold deposited on silver the Au(100)-(5x1) was observed after an average thickness of 3 M-L was deposited.⁽¹⁶⁷⁾
- 5) For gold deposited on platinum an Au/Pt(100)-(7x1) was observed after 5 M-L was deposited.
- 6) For gold deposited on a gold surface exhibiting an Au(100)-(5x1) pattern an Au(100)-(1x1) was observed until the substrate temperature was raised to 0°C when the (5x1) returned.⁽¹⁶⁷⁾

The Pt(100)-(5x1) pattern is an approximate description and stems from the early observations with very low resolution

LEED instruments. At moderate resolution, as was used in this investigation, splitting from the $(0,n/5)$ positions was observed. The true (5×1) described by Lyon was not sufficient to account for this case. At higher resolution, Palmberg resolved further spots and, from a single domain pattern, determined that the coincidence mesh size was $Pt(100) - (\sqrt{29} \times \sqrt{170})$. This mesh is shown in Figure IV.1; there are 4 possible domains. The B.P. group⁽¹⁹⁷⁾ has produced very clear patterns agreeing with this mesh size. By modifying the ideas of Fedak and Gjostein, and Morgan and Somorjai that a hexagonal overlayer may be formed, the following model is proposed, in collaboration with the B.P. group. A hexagonal overlayer similar to a normal $Pt(111)$ arrangement is formed closely above an undistorted $Pt(100) - (1 \times 1)$ atomic arrangement so that the required coincidence of $(\sqrt{29} \times \sqrt{170})$ occurs. The nearest approach of the atoms in an undistorted $Pt(111)$ net to a $Pt(100)$ net was seen with the following near coincidences

$Pt(100)$	$Pt(111)$	
0,0	0,0	defined coincidence
-1,13 $(\sqrt{170})$	-1,13	All measured in base mesh (100) unit vectors.
5,2 $(\sqrt{29})$	6,5	
4,15	5,18	

The $Pt(111)$ mesh was then distorted to make the above atomic positions coincide. This was achieved by compressing the $Pt(111) - (1 \times 1)$ from the normal mesh size of $2.774\text{\AA} \times 2.774\text{\AA}$ with a lattice vector angle of 120° (Wood's notation⁽²⁸⁾) to $2.674\text{\AA} \times 2.678\text{\AA}$ with vector angle 119.13° . The angle between

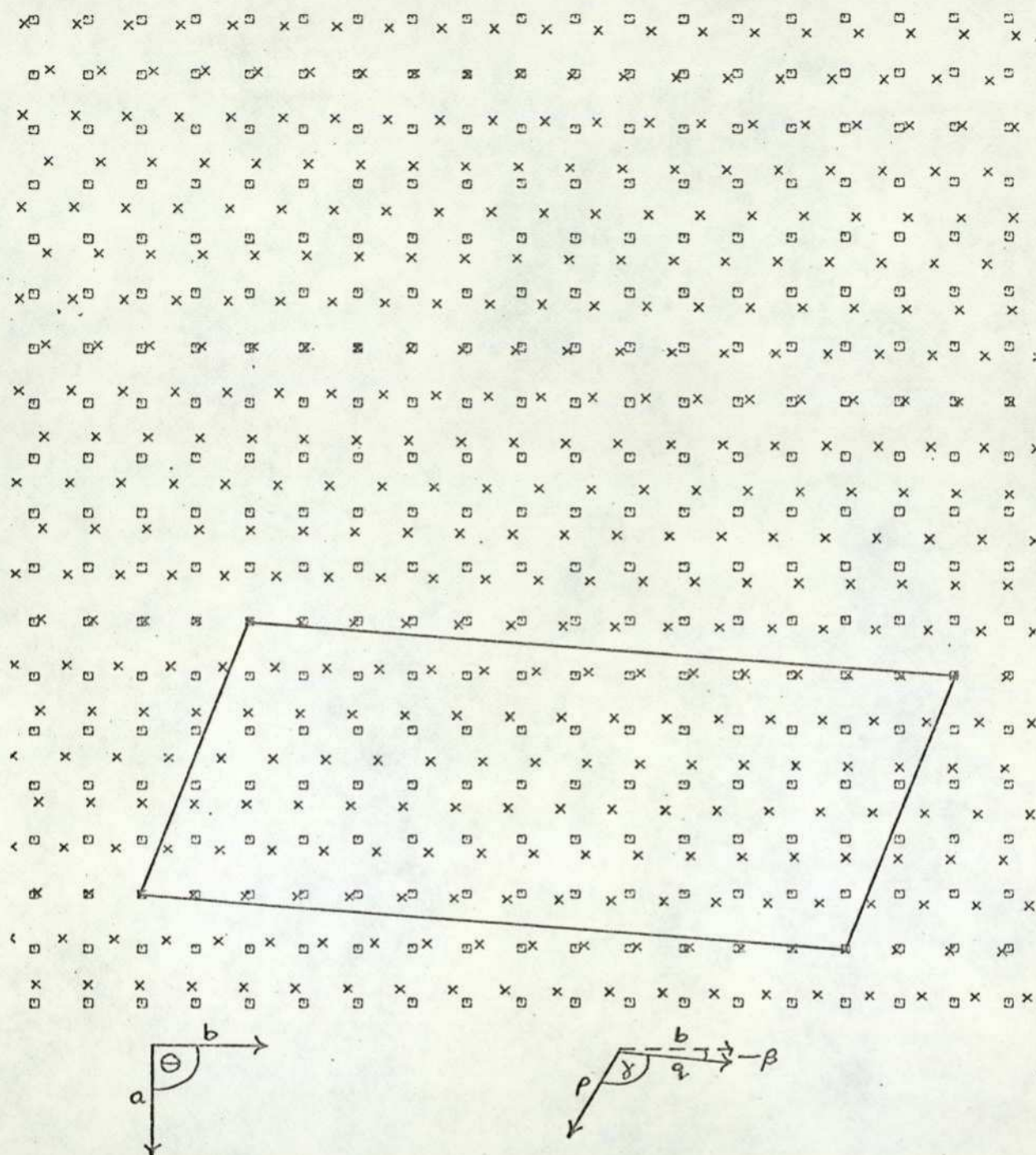
the $2.674\text{\AA}$ vector of the overlayer and the $2.774\text{\AA}$ Pt(100) substrate vector was 0.71° . This surface mesh contraction of 3.5% is similar to that required (4.3%) to fit a hexagonal mesh on the Au(100) mesh. The coincidence mesh is shown in Figure IV.1.

This hexagonal overlayer model is plausible in accounting for the appearance of the Pt(100)-(5x1) pattern for the following reasons.

Prolonged oxygen treatment, normally an effective method of producing a Pt(100)-(5x1) surface structure, may also give rise to a 12 spot pattern attributable to two domains of a Pt(111)-(1x1) surface structure in addition to a Pt(100)-(5x1).

When the mesh of Figure IV.2 was drawn by a computer plotter on triacetate paper, photographic reduction using a microscope enabled laser simulation of the LEED process to be carried out. This method, described by Cambell and Ellis⁽¹⁹⁸⁾ produced a pattern of very similar intensity to the moderate resolution diffraction patterns e.g. Figure III.22a,c. Further resolution was not obtained due to laser speckle.

The hexagonal overlayer model matches the observation that the Pt(100)-(5x1) structure is associated with relatively smooth surfaces compared with appearance of the Pt(100)-(1x1). If a complete (111) monolayer of mesh dimensions as above rearranges to the less densely packed (100) mesh there must be an exclusion of surface atoms equivalent to 23% of a (100) monolayer. These must contribute to a rough surface on an



■ Base Mesh

$$a = 2.774 \text{ \AA}$$

$$b = 2.774 \text{ \AA}$$

$$\theta = 90.0^\circ$$

x Surface Mesh

$$p = 2.678 \text{ \AA}$$

$$q = 2.674 \text{ \AA}$$

$$\gamma = 119.8406^\circ$$

$$\text{Angle between vectors } q \text{ and } b (\beta) = 0.7958^\circ$$

FIGURE IV.1 The $(\sqrt{29} \times \sqrt{170})$ Coincidence Mesh between slightly distorted Pt(111) and Pt(100).

atomic scale.

In this model the coincidence mesh is taken as ($\sqrt{29} \times \sqrt{170}$) from the determination by Palmberg. However, the importance of these exact dimensions is not clear and it seems probable that many similar coincidence patterns also co-exist. Modifications in the $\sqrt{170}$ coincidence lattice vector to surrounding points, $\sqrt{145}$ or $\sqrt{197}$ would be difficult to detect in the LEED pattern. If a mixture of such meshes existed within the area of the electron beam a diffuse mixed pattern would result. The difference would not be detectable in a poor resolution instrument but would be seen with high resolution. The B.P. group⁽¹⁹⁷⁾ has observed such a pair of diffraction patterns on Pt(100) with a true ($\sqrt{29} \times \sqrt{170}$) appearing only after annealing above 1100°C.

The major problem with this explanation lies with the cause. Although a reduced surface energy will result from the conversion of a (100) plane to a (111) plane due to closer packing, what is so special about ($\sqrt{29} \times \sqrt{170}$)? If the (111) mesh is perfectly flat and close to the (100) substrate the separation of atoms in the two layers varies across the mesh. The interlayer spacing (d_i) in the case of atoms at the corners of the coincidence mesh, and $(\frac{1}{2}a^2 + d_i^2)^{\frac{1}{2}}$ for a (111) atom centrally spaced between the (100) atoms (spacing 'a') represent the two extremes of interatomic spacing. For the possible case that the interlayer spacing is the close packing separation, 'a', the two extremes of substrate (100) - overlayer (111) atomic separation become 'a' and ' $\sqrt{\frac{3}{2}}a$ ', a difference of 23%. Unless unusually long range forces

operate, these varying interatomic spacings will equalise by surface buckling effects or by creating vacancies in the (111) overlayer at points where excessive interatomic stresses would exist.

In a surface buckling model the atomic movements to revert to the bulk (100) surface are small and could occur at the low temperatures observed (i.e. room temperature adsorption of carbon monoxide). However, a vacancy model would remove the need to 'lose' 23% of a (100) monolayer.

The vacancy model fits experimental data in one important area. The LEED pattern of a Pt(100)-(5x1) shows the (0,n/5) spot groups as lower or similar in intensity to the (1,0) and (1,1) spots. If a complete (111) monolayer exists as shown in Figure IV.1 the diffraction pattern would be predominately Pt(111)-(1x1) with additional spots. This situation is only observed after extensive oxygen treatment. Vacancies in the (111) mesh allow the atomic positions of closest approach to be avoided, they enhance the (100) mesh reflections at the expense of the (111) mesh, and they allow the Pt(111) overlayer to contain the same atom layer average density as the (100) substrate.

The energy difference between the two surface structures is small, as shown by the ease of transformation caused by gas or metal adsorption at room temperature to form the (1x1) and annealing treatment to $>700^{\circ}\text{C}$ to regain the (5x1). The two groups of short range forces that change with surface structure are the interatomic forces within the layer which cause close packing (111) and the interlayer forces which

continue the bulk atomic arrangement to the surface. These forces are apparently very similar and are unbalanced by the presence of impurities. This balance favours hexagonal growth more strongly in the gold crystal where the Au(100)-(5x1) forms above 0°C.

The occurrence of reorientation is more plausible if impurities are shown to be present. Edmonds, McCarroll and Pitkethly⁽³⁾ showed the sulphur impurity cause of the Ni(111) → Ni(100) surface transformation. Ion emission from the Pt(100) crystals indicated that throughout the work alkali metals remained in the crystals. However, ion emission only occurred above 1000°C and may have reflected bulk levels while A.E.S. was carried out below 300°C. No correlation was made between these ion levels, necessarily at high temperature, and A.E.S. detected levels. Many studies have shown that no impurities may be detected by A.E.S. when the (5x1) pattern is obtainable. However, the potassium peak at 252 eV may not easily be resolved from the 251 eV platinum peak; the sodium peak at 981 eV occurs towards the higher noise end of the commonly scanned range of A.E.S. Calcium was clearly detected at 292 eV on platinum crystals and foils in this study. McCarroll, Edmonds and Pitkethly⁽¹⁾ have proposed that alkali metals lie between the (100) and (111) layers and are difficult to detect as the impurities are screened by the top Pt(111) layer which reduces the calcium signal and represent only 10 - 20% of a monolayer. They also proposed, backed by some experimental evidence, that the electron beam of the

detecting probe effectively removed the calcium from the surface.

Attributing the Pt(100)-(5x1) to the presence of alkali metals is subsequently difficult to prove if the most sensitive technique for surface impurities, A.E.S., causes the contamination to disappear. The X-ray photo electron spectroscopy method, which creates the initial core holes using X-rays may answer this question unless X-rays or the low secondary electron current in the surface of crystals also remove the alkali metal before it is clearly detected.

Grant and Haas, who are the only workers who have reported a clean surface Pt(100)-(1x1) pattern, appear to corroborate the above arguments. Their (1x1) pattern was achieved after prolonged annealing in a high current beam of argon ions, followed by annealing at 1100°C. If the crystal was cooled from 1200°C in oxygen the (5x1) appeared strongly and could not be returned to a clean (1x1) without an acid etch. Although this fits the requirement to remove alkali metal near the surface it is probable that a prolonged etch loads the surface with sulphur or chlorine, both of which cause an initial change to (1x1) by a surface exhibiting a Pt(100)-(5x1).

The experimental results and discussions above indicate that the Pt(100)-(5x1) diffraction pattern results from a clean surface while the primitive (1x1) pattern is associated with surface impurities. However the failure of A.E.S. to detect impurities in either case after cleaning procedures does not eliminate the possibility of an impurity stabilised

(5x1). The impurity may be initially below the detection limit of the A.E.S. method or modified in the electron beam used in the method.

IV.2 R.F. Heating in Vacuum Systems

R.F. induction heating was used successfully in this work. When a molybdenum work coil was fitted with cooled copper feedthroughs the system pressure could be maintained well in the U.H.V. range while operating. It should be possible to obtain the lowest pressure of any method when heating by fabricating a work coil of tubing with circulating coolant. The use of the crystal manipulator and sample mounting were simplified by using R.F. heating, avoiding the need for heavy current connections to the crystal. The R.F. work coil was a useful reference point to ensure reproducible evaporation from the source.

The serious disadvantage found in this work was the need to envelope the sample in the coil during heating. The considerable movement required between the LEED and A.E.S. positions into the coil was difficult and time consuming. The return movement to the electron optics centre of curvature was also very exacting. Sample heating could be carried out simultaneously with evaporation but not with LEED or A.E.S. operations. The effects of annealing on A.E.S. or LEED properties would be determined most rapidly by resistive or radiation heating methods; these methods are essential for studies of hot surfaces.

IV.3 Condensation Coefficient

Unless the surface coverage of an evaporated metal film is determined after condensation it must be estimated using some assumption of the condensation coefficient. If an ionisation monitor or Knudsen source is used the flux incident on the substrate may be determined. The average coverage is then the product of flux and condensation coefficient integrated over the evaporation time. When interference techniques, microbalance, or quartz crystals are used the ratio of deposition on the monitor to that on the sample must be determined. However, for metals evaporated on metals the condensation coefficient may generally be taken as unity (Bauer⁽¹⁹⁹⁾). In some cases the adsorbate forms a "hot" adsorption layer in which the arriving atoms are highly mobile and have a finite chance of evaporating from the surface. The condensation coefficient in such a case is dependent on the number of film nucleation points or impurity sites on the surface. The growth of surface layers when high mobility occurs is then in complete monolayers. This appears to be the case for silver evaporated on nickel (Jackson, Gallon and Chambers⁽¹⁴⁵⁾) where reduced condensation coefficients were proposed. A unity coefficient associated with low surface mobility, was taken to occur for copper evaporated onto platinum(100) at 20°C where statistical epitaxial growth appeared to occur. On the Pt(111) crystal, where the copper growth was disordered at 20°C, sufficient mobility for ordered epitaxial growth occurred at 400°C.

However, the condensation coefficient determined by the rate of rise of the copper Auger signals with recorded evaporation of copper in poorly calibrated deposition conditions was reduced relative to condensation onto a 20°C substrate.

IV.4 Surface Structures; Copper on Platinum

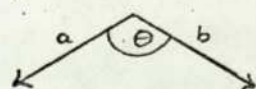
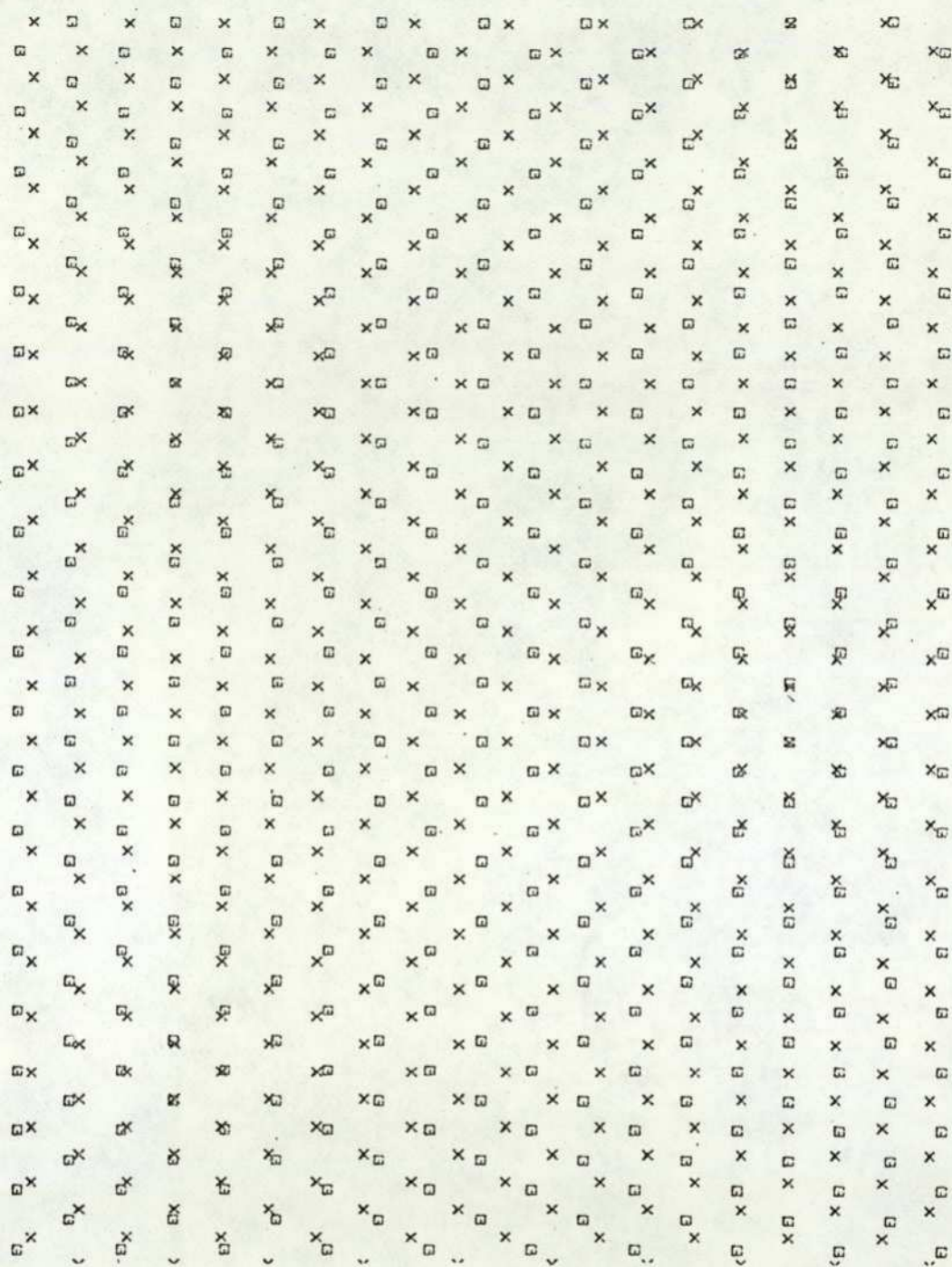
IV.4.1 Copper on Pt(111)

Growth of copper on the Pt(111) crystal face, when a low evaporation rate was used, occurred as an amorphous disordered overlayer. Island growth of bulk copper areas would be characterised by the development of diffuse spots at positions corresponding to the new atomic spacing while the substrate spots would become diffuse and weaker as the island surface area was increased. The appearance of coincidence lattice beams resulting from an undistorted Cu(111) lattice growing epitaxially on the Pt(111) crystal would be based on 'n' platinum base lattice meshes where:

$$n(\text{Pt closest spacing}) = (n+1) (\text{Cu closest spacing})$$

$$n = \frac{2.556}{2.774 - 2.556} = 11.7$$

These superimposed meshes are shown in Figure IV.2. No true coincidence lattice may occur until very large mesh sizes are reached. At a distortion of the copper mesh by +0.38% a coincidence at 12 substrate unit mesh units will occur. No such pattern was observed in this work. The failure to clearly observe multiple scattering from the two meshes was

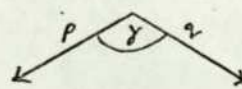


Pt(111)

$$a = 2.774 \text{ \AA}$$

$$b = 2.774 \text{ \AA}$$

$$\theta = 120^\circ$$



Cu(111)

$$p = 2.55 \text{ \AA}$$

$$q = 2.55 \text{ \AA}$$

$$\gamma = 120^\circ$$

FIGURE IV.2 A Cu(111) mesh superimposed on Pt(111).

unlikely to be due to attenuation of the signal from the substrate. Taylor⁽¹⁸⁷⁾ has described multiple scattering due to 1-2 atomic layers of copper on tungsten.

Copper on platinum was found to gain sufficient mobility to allow rearrangement to epitaxial layers when annealed at 400-450°C. At higher temperatures, although rearrangement occurred more rapidly, the copper was partially lost from the surface by diffusion into the bulk or, above 800°C, by evaporation and diffusion.

The conditions under which the transformation from pseudomorphic copper at the platinum spacing to the bulk copper spacing in the 2 - 5 M-L films occurred were not investigated. Maintaining a crystal temperature of 400-450°C was sufficient to allow the copper atoms to move from the initial positions characteristic of platinum to the bulk copper positions. The incident copper flux provided the supply of atoms required to fill in gaps which would occur if a monolayer of copper at the platinum spacing reverted to copper spacing. The difference in surface atom density per monolayer between the Pt(111) (1.501×10^{19} atoms m^{-2}) and Cu(111) (1.768×10^{19} atoms m^{-2}) is 18% of the platinum density and represents the area uncovered by the conversion from the platinum to copper surface spacing.

A graph of Auger signal plotted against copper deposition, of the form shown in Figure III.16, may be drawn for a series of depositions. If very small increments in copper thickness are made the growth characteristics may be determined. In the submonolayer range there have been no reports

of any variation of A.E.S. response from identical surface coverages of materials differing in surface geometry. The theory of Bishop and Riviere⁽¹⁰⁶⁾ does not consider the exact geometry, and the results of Ibach, Hom, Dorn and Luth⁽¹³⁸⁾ do not rely on structure.

However, the growth mechanism dependence in thicker films is detectable using the theory of Gallon⁽¹⁴³⁾. When a transition from one growth orientation to another occurs a discontinuity will occur in the Auger signal/deposition graph. The reduction of 18% in the copper film area due to the collapse of the pseudomorphic growth of a monolayer of copper on platinum will not change the copper Auger signal. The signal from the substrate, which had been attenuated by the copper overlayer may be expressed as:

Substrate signal(1 M-L copper at Pt(111) spacing) = $T_1 I_0$
 where T_1 is the transmission factor through the pseudomorphic monolayer.

I_0 is the substrate Auger signal with no overlayer absorption.

This expression assumes no loss of incident beam energy on passage to the substrate. If the surface copper rearranges to bulk copper spacing the substrate signal will have two components

$$I_s = 0.82 I_0 T_2 + 0.18 I_0$$

where T_2 is the transmission factor through the copper monolayer at bulk copper spacing.

When the initial coverage was greater than 1 pseudomorphic monolayer the possible island structures gave an

infinite number of similar equations. The form of the discontinuity should be seen in a series of experiments of Auger response from the substrate after small increments of copper coverage. As in all quantitative Auger calibrations the transition would be most clearly observed in a system in which repeated scans of the spectrum were made during metal deposition. Such a method would only be easily conducted in a cylindrical mirror analyser system.

IV.4.2 Copper on Pt(100)

The first observation of the variation of copper Auger signal with surface geometry detected by LEED was the 50% increase which occurred on leaving the copper covered dirty platinum (100) crystal overnight. This change was not due to inherent variation in instrumental response which had been found to be constant to within $\pm 10\%$ from 1-3 M-L copper films when recorded over a 3 day period.

In the later quantitative evaporations of copper on Pt(100) the normal repeatability was improved to $\pm 5\%$ by careful attention to maintaining constant A.E.S. conditions. The copper signal enhancement was shown to occur after deposition onto an oxygen or sulphur covered surface or when a heavy deposition on a clean surface was subsequently exposed to oxygen.

Two possible explanations for this behaviour were considered:- an electronic effect or structural effects. The anticipated electronic effect was the modification of intensity of peaks due to Auger transitions involving the copper valence band. The spectra obtained by running the

instrument in its standard mode showed insufficient detail to determine the origin of the broad peaks. After the higher resolution method was developed copper spectra were obtained from both clean and contaminated surfaces. No clear differences were observed. The modification of the low resolution spectra by the proportions observed could not be assigned to changes in the surface electronic properties.

The results from the growth of copper films of increasing thickness on the Pt(100) crystal showed that above 0.8 M-L of copper the A.E.S. spectra of the major copper peaks in the range 720-940 eV were identical in shape to spectra from bulk copper. Any differences at lower copper coverage could not be clearly detected due to loss of signal in noise.

The anomalous high copper Auger signals were associated with changes in surface structure. The Pt(100)-(2x2)-Cu and Pt(100)-($\sqrt{2}\times\sqrt{2}$)R45°-Cu patterns, both of which were associated with sulphur and oxygen impurities, gave A.E.S. signals above the clean surface calibration line. The substrate signals did not change considerably during changes of copper signal but were low values with a relatively high noise background. Impurities in the surface copper were expected to decrease the copper signal due to absorption of both incident and secondary electrons. No mechanism for enhancing the signal could be clearly determined. The following possibilities are discussed.

- 1) The well ordered surface layer detected by LEED caused a high signal from the surface where no subsequent absorption of Auger electrons could occur. This effect could not explain

the enhancement by up to 50%.

2) If true layer growth only occurred in the presence of impurities the signal from the surface copper would be higher than the same quantity of copper arranged as islands. The A.E.S. signal from copper at the centre of the islands would be absorbed by outer layers of copper. Similarly, transitions from island growth to layer growth would result in reduction of substrate signal. To account for a typical experimentally observed 25% increase in copper signal from a thick film of copper an island structure of 80% coverage would be required to increase to continuous (i.e. 100%) layer coverage. The substrate signal corresponding to the island growth would have been ~20% of the clean substrate signal. However, the observed initial substrate signal was lower than this (~10%) and was unchanged during the transition.

3) The impurities formed a regular structure as determined by LEED and this ordered structure caused less absorption of the incident beam reaching the platinum substrate. This beam may have included strongly forward scattered components. The resulting high backscatter current from the larger platinum atoms may cause a copper signal enhanced above that due to a thick copper film. This description is in accord with Gallon's⁽¹²⁷⁾ observations. The effective signal boost due to backscatter enhancement could explain the increased signal observed.

The variation of A.E.S. signal from the copper depending on the structure of the surface film is of importance in

the application of A.E.S. for quantitative analysis of the surfaces of alloys. The signal from the element depended not only on the numerical densities of the copper atoms in the surface layers but on the relative positions of the atoms. Insufficient data were obtained to determine the nature of the effects.-

IV.5 Quantitative A.E.S.; Copper on Pt(100)

IV.5.1 The A.E.S. Signal from Copper on Platinum

The results shown of the growth of the copper Auger signals with increasing copper deposition contain information both of the inelastic mean free path of electrons in copper and the growth mechanism of the copper film. Allowance must be made for the interdependence of these factors.

If it is assumed that the growth occurred as homogeneous, infinitely thin, layers the copper signal, I_c , from the copper film as a ratio of that from a bulk copper crystal $I_{\infty Cu}$ will be (Seah⁽¹⁴⁹⁾):

$$\frac{I_c}{I_{\infty Cu}} = 1 - \exp(-n/n_c)$$

where n is the copper film thickness causing current I_c and n_c is the inelastic mean free path for copper^{Auger} electrons in the copper film.

This was applied to the data of Figure III.27 in the form

$$\frac{1}{n_c} = \frac{-1}{n} \log_e \left(1 - \frac{I_c}{I_{\infty Cu}} \right)$$

The value of $I_{\infty Cu}$ for each peak was taken as the value

determined at 12 M-L. The unit of thickness measurement used was the spacing between (200) planes in the face centred cubic copper crystal. This represents a surface density of 1.54×10^{15} atoms per monolayer.

At a coverage corresponding to 1 M-L the copper peaks gave the following values for n_c , the inelastic mean free path.

Peak	n_c (M-L)	n_c (corr1)
927 eV	2.35	5.67 Å
847	2.20	5.30
774	2.36	5.69

where n_c (corr1) is the inelastic mean free path in Angstroms (1 M-L is equivalent to 1.808 Å) corrected for the oblique exit paths for Auger electrons accepted by the retarding field analyser. (Seah¹⁴⁹).

The platinum substrate signal at 239 eV was also measured and n_c determined from:

$$\frac{I_{Pt}}{I_{\infty Pt}} = \exp(-n/n_c)$$

$$\text{i.e. } -\frac{1}{n_c} = \frac{1}{n} \log_e \left(\frac{I_{Pt}}{I_{\infty Pt}} \right)$$

$$n_c = 1.80 \text{ M-L}$$

Correcting this as before, the escape depth of the 239 eV electrons in copper was 4.34 Å.

The calibration graph, Figure III.27, shows that considerable deviation from exponential signal dependence occurred in this case. The film thickness 'n' was then plotted against $\log_e(1 - I_c/I_{\infty Cu})$ from the calibration graph and the gradient

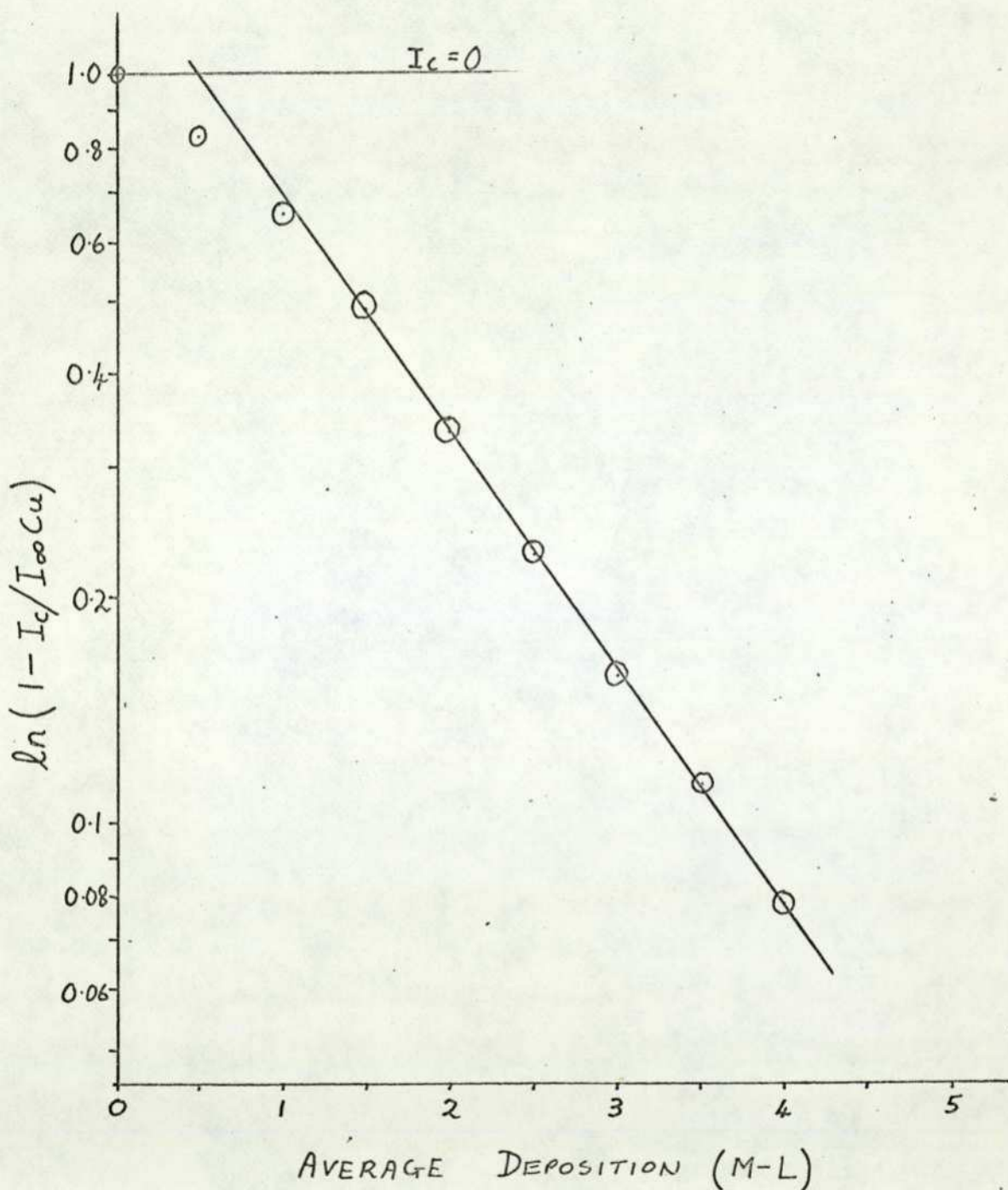


FIGURE IV.3 The Copper 927 eV Auger electron signal versus copper film thickness graph (III.27) is redrawn here to show the region of exponential signal growth (<1.25 M-L) and reduction of effective deposited film by 0.5 M-L.

of the straight line portion obtained as the mean free path over that range of film thickness of copper.

The calibration line for 927 eV electrons in copper has been drawn with these axes in Figure IV.3. A transition period occurred in the range 0-1.25 M-L before true exponential signal was recorded. The gradient of this line, equal to the inelastic mean free path, was then 1.43 M-L. At normal incidence this value would be corrected to 3.45 Å. The intercept on the film thickness axis at zero copper signal, i.e. $\log_e(1-I_c/I_\infty \text{Cu})=1.0$, of the extrapolated straight line section was at 0.50 M-L. This result again confirms the lack of mobility of the copper on the platinum surface. The random arrival of the evaporant caused the formation of surface pinnacles and bald patches on an atomic scale in the film. The reduced Auger signal from thinner areas of film was not compensated by the increased signal from thicker areas when compared with a uniform film of the average thickness. This effect was then quantified as equivalent to a $\frac{1}{2}$ M-L reduction in film thickness for depositions of 1.25 M-L of copper.

IV.5.2 A Detailed Growth Mechanism for Copper on Pt(100)

In the previous discussions the copper overlayers have been considered as growing with no discrete unit size. However for signal absorption with a mean free path of ~ 2 M-L the probability of an Auger electron escaping is determined by the statistics of the coverage of each surface site. If the surface has "N" atom sites per unit area and "m" atoms are deposited randomly on the area the probability, $P(r)$, of a site having

"r" atoms (in a column) on it is (Lawrence⁽²⁰⁰⁾),

$$P(r) = \exp(-m/N) (m/N)^r \frac{1}{r!}$$

Then $P(0) = \exp(-m/N)$

$$P(1) = \exp(-m/N) \cdot (m/N)$$

$$P(2) = \frac{1}{2} \exp(-m/N) \cdot (m/N)^2 \quad \text{etc}$$

$$P(3) = \frac{1}{3} P(2) \cdot (m/N)$$

For many sites (1.3×10^{19} atoms m^{-2}) $P(r)$ is the fractional coverage with an atomic column height 'r' at an average coverage of (m/N) monolayers. Several values of the proportion of the surface with depletion or enhancement from the average layer thickness are shown in Table IV.1. At the 1 monolayer average thickness point 37% of the substrate surface is uncovered and 37% has the average thickness of 1 monolayer. There are pinnacles of 5 atoms height over 0.3% of the surface. This mode of growth seriously changes the probability of escape for the Auger electrons.

IV.5.2.1 Model for Auger Signal Growth from Static Adatoms

In this model a fraction "A" of the incident electron beam is considered to be transmitted through each atomic layer of the copper film. Similarly, a fraction "B" of the Auger current will pass through each atomic layer on its way to the surface. For a standard electron beam incident on a layer of atoms an Auger signal "S" is formed in that layer to be collected, if not subsequently attenuated, by the analyser system.

The collected signal from bulk copper (or a very thick overlayer film) is then made up by:-

Average deposited coverage		0.1	0.3	0.5	1.0	1.5	2.0	2.5	3.0
Monolayers on fraction of surface		Resulting fractional coverages							
C_0	0	.905	.741	.607	.368	.223	.135	.082	.050
C_1	1	.091	.222	.303	.368	.335	.271	.205	.149
C_2	2	.005	.033	.076	.184	.251	.271	.257	.224
C_3	3	.	.003	.013	.061	.126	.181	.214	.224
C_4	4	.	.	.002	.015	.047	.090	.137	.168
C_5	5	.	.	.	.003	.014	.036	.067	.101
C_6	6	.	.	.	.001	.004	.012	.028	.050
C_7	7	.	.	.	.	.001	.003	.010	.022
C_8	8	.	.	.	.	.	.001	.003	.008

TABLE IV.1

Characteristics of Static Adatom Film Growth

Example of above coverages : A 1 M-L average deposition

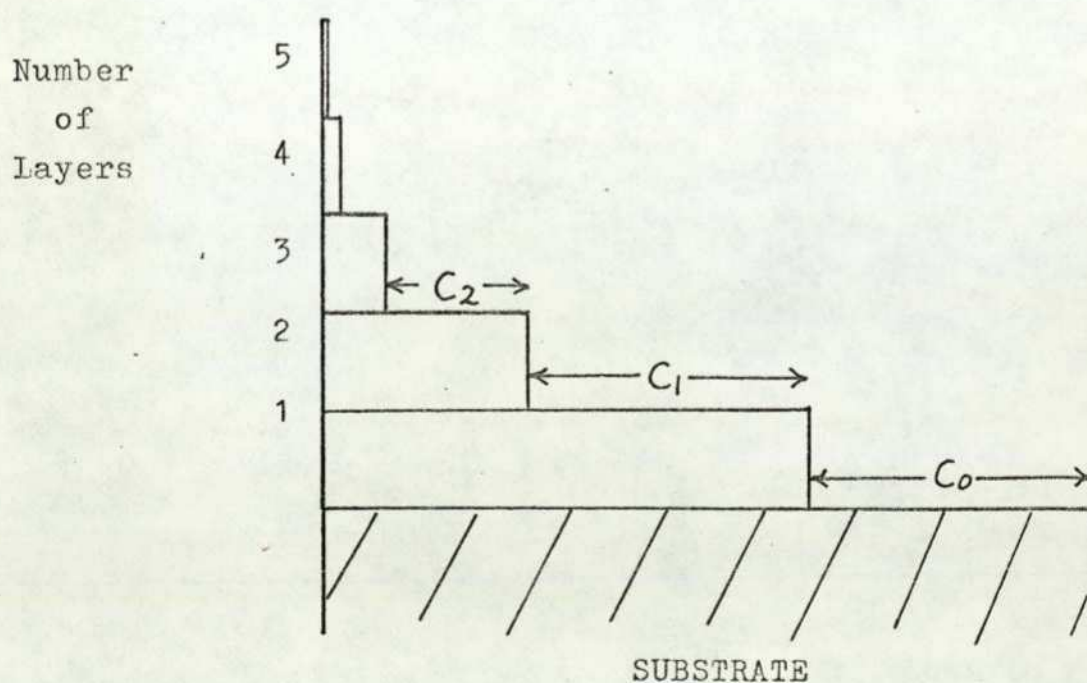


FIGURE IV.4

Signal from top (1st) layer = S

Signal from next (2nd) layer = S.A.B.

Signal from next (3rd) layer = S.A².B².

A.B. may be combined to give a transmission "T" for the total path for exciting electrons travelling into the surface and Auger electron leaving.

The total signal, I_∞, from bulk copper is then

$$I_{\infty} = S (1 + T + T^2 + T^3 \dots\dots)$$

$$\text{As } |T| < 1$$

$$I_{\infty} = S / (1 - T)$$

For a thin film growing with layer sizes given by Table IV.1 the fractional coverage of surface layer copper is (1-C₀) and will contribute (1-C₀)S to the output signal. The next layer, covered by one overlayer has a fractional coverage of (1-C₀-C₁) and will contribute (1-(C₀+C₁))TS. The total signal from a film is then

$$I_f = (1-C_0)S + (1-(C_0+C_1))TS + (1-(C_0+C_1+C_2))T^2S \dots\dots$$

$$= S \left(\frac{1}{1-T} \right) \left[1-C_0-TC_1-T^2C_2-T^3C_3 \dots\dots \right]$$

For comparison with experimental results the ratio of I_f/I_∞ has been taken with I_∞ being the signal from a >6 M-L film.

$$\text{Then } I_f/I_{\infty} = 1-C_0-TC_1-T^2C_2 \dots\dots$$

The measured value of I_f/I_∞ for 927 eV electrons in copper at 1 M-L deposition was 0.355. By numerical substitution the value of T was 0.57. However by substituting this value for T into this equation with 2 M-L deposition the relative Auger signal, I_f/I_∞ should be 0.58. The measured value at 2 M-L was 0.68.

The mean free path (n_c) calculated from Gallon's formulae corresponding to the 1 M-L experimental value of $I_f/I_\infty = 0.355$ in this model is

$$1 - 0.355 = \exp(-1/n_c)$$

$$\text{Then } n_c = 2.28 \text{ M-L}$$

The value of n_c derived from T directly is

$$0.57 = \exp(-1/n_c)$$

$$\text{Then } n_c = 1.78 \text{ M-L}$$

This value of n_c then results in I_f/I_∞ (2 M-L) = 0.675.

This closely matches the experimental value of 0.68. As was shown in Figure IV.3 the copper signal growth reverts to exponential dependence above ~2 M-L.

The characteristic copper growth on Pt(100) thus appears to follow the static adatom growth model for the first monolayer deposited when increasing mobility allowed relaxation to layer growth. This growth of signal with deposition rose more quickly than exponentially.

The signal from the substrate fell consistently as an exponential curve. The transmission factor, T, for 239 eV electrons through a single monolayer of copper for this curve was 0.46 corresponding to an electron mean free path of 1.29 M-L if the static adatom applied. For true monolayer growth this signal at 1 M-L indicated the electron mean free path of 1.80 M-L.

IV.5.3 Annealed Copper Films

The A.E.S. spectra derived from copper films on the Pt(100) crystal which had been annealed at 400-600°C during or after deposition were compared with the calibration graph for

copper deposition on Pt(100) maintained at room temperature. These results were described in section III.5.2.3 and present further evidence for the initial growth mechanism differing from complete monolayer development. On annealing the pinnacles which grew during the random arrival of evaporant onto the substrate may have redistributed to complete monolayers by surface diffusion. The model described above to explain the A.E.S. signals detected during film growth is used here.

For a static adatom film of 1.0 M-L average deposit of copper the substrate signal, as a fraction of the zero coverage signal, will change from

$$\begin{aligned} I_f/I_\infty \text{ static} &= \exp(-1.0/1.80) \\ \text{adatom} &= 0.57 \end{aligned}$$

$$\begin{aligned} I_f/I_\infty \text{ monolayer} &= \exp(-1.0/1.29) \\ \text{growth} &= 0.46 \end{aligned}$$

The results obtained from annealed films are in qualitative agreement with the growth characteristics expected from true monolayer growth if the room temperature deposition results are attributed to static adatoms.

IV.6 Gas Adsorption on Clean and Copper Covered Pt(100)

These gas adsorptions were carried out in this system to allow direct comparisons to be made between the clean surface and various copper overlayers. Although the results for these gases have been widely published, direct comparison between systems is invalid due to different errors in measur-

ing true gas pressure and surface cleanliness.

The undetectably low rate of oxygen adsorption on the cleaned crystal confirmed the crystal cleanliness from the evidence of Weinberg, Lambert, Comrie and Linnett⁽¹⁶⁹⁾.

IV.6.1 Oxygen Adsorption

Oxygen was found to adsorb readily on all copper overlayers. The A.E.S. measurements showed that the signal characteristics were very similar, within 10%, for copper overlayers of both 1 and >5 M-L. If the >5 M-L layer is assumed to adsorb as a bulk crystal the adsorption by 1 M-L also appears to act as the surface of a homogeneous bulk crystal. This is in accord with the results given earlier (section III.8.9) that the Auger spectra from the copper surface have the characteristics of a thick film at ~ 1 M-L.

The LEED patterns associated with oxygen adsorption on, or incorporation in, the copper film were the Pt(100)- $(\sqrt{2} \times \sqrt{2})R45^\circ$ -Cu/O and the Pt(100)- $(\sqrt{2} \times \sqrt{13})$ Cu/O. The Pt(100)- $(\sqrt{2} \times \sqrt{2})$ -Cu/O occurred at low temperature (20°C) when no major surface rearrangements took place. The more complex Pt(100)- $(\sqrt{2} \times \sqrt{13})$ -Cu/O type patterns, because of the method of formation, are assumed to incorporate oxygen. The intensities of the diffraction patterns showed that the coincidence mesh was made up largely of Pt(100)- $(\sqrt{2} \times \sqrt{2})R45^\circ$ units. This pattern was confirmed as due to a reorientation by the action of H_2S . As is described later, H_2S adsorption caused desorption of other adsorbed gases to form the characteristic H_2S pattern. In this case the Pt(100)- $(\sqrt{2} \times \sqrt{13})$ -Cu/O pattern was strengthened by the H_2S .

The adsorption of oxygen on the pseudomorphic copper films on Pt(100) was similar to that ^{on the surface of bulk copper} reported by many other workers (section I.2.3.11). The Cu(100)-(2x4) observed by Lee and Farnsworth⁽⁷¹⁾ and Ertl⁽⁷²⁾ was ^{not} seen in this work. The oxygen treatments were insufficiently severe to cause complete oxidation of the surface film to form a bulk oxide structure. In a simple adsorption system the Pt(100)-($\sqrt{2} \times \sqrt{2}$)R45-0 pattern corresponds to an oxygen surface coverage of $\frac{1}{2}$ M-L, which, at the Pt(100) spacing, is 6.5×10^{14} atoms cm^{-2} .

IV.6.2 Hydrogen Sulphide Adsorption

The adsorption of sulphur on the clean and copper covered surfaces was extremely rapid. The scatter of the data points at exposures to H_2S of greater than 10 L resulted from the experimental difficulty of maintaining constant incident electron beam current during the rapid poisoning of the filament.

The A.E.S. results were in agreement with the LEED patterns obtained from the surfaces. On Pt(100) the ($\sqrt{2} \times \sqrt{2}$)R45⁰, which formed on exposure to H_2S , corresponded to a surface atom coverage of 50%. From Figure III.40 the sulphur Auger signal magnitude was measured as 147 in the arbitrary units of peak to peak distance in the plotted differential of the electron energy distribution. The measured signal has been corrected by subtracting the clean surface Pt 150 eV peak size. This caused a slight underestimate of the sulphur signal as the signal enhancement from the substrate was reduced by the surface sulphur.

The data required to determine the magnitude of this effect was not taken. However, using the data from Rivière⁽²⁰¹⁾ that the mean escape depth for electrons of 150 eV energy is 5 Å the reduction in substrate signal in this case was calculated from

$$I_n = I_o \exp(-t/t_c)$$

where

I_n is substrate signal through the overlayer

I_o is the original substrate signal

t is the overlayer thickness

t_c is the inelastic mean free path for substrate Auger electrons through the overlayer.

The value of t_c used here was reduced to 75% of the measured value in order to allow for the collection efficiency of the retarding field analyser system (Seah⁽¹⁴⁸⁾). The value of t , the effective thickness of the sulphur monolayer on the Pt(100) substrate, was taken as 2.7 Å. The sulphur atoms were assumed to take up an f.c.c.(100) epitaxial layer with interlayer spacing of (unit cell dimension)/2.

$$\text{Then } I_n/I_o = \exp(-2.7/3.75) = 0.49$$

The absorption of the platinum signal by the half coverage surface sulphur was then 25% of the clean surface value. This was small compared with the scatter of the sulphur signal points. The initial clean surface signal may have also included a small sulphur impurity signal due to persistence of sulphur in the vacuum system.

The signals resulting from H₂S absorption on the Pt(100) crystal with a ~1 M-L copper film evaporated on it are shown

in Figure III.41. The signal attributable to sulphur in this case is 93 units (under identical conditions to those used for clean surface case). The LEED pattern corresponding to this, a Pt(100)-(2x2)-Cu/S, indicated a 25% surface coverage.

The ratio of Auger currents from the clean and copper covered platinum crystal was $147/93 = 1.58$. The LEED patterns, at the simplest analysis, indicated a ratio of 2.0. However, the $(\frac{1}{2}, \frac{1}{2})$ spots are common to each LEED pattern; small areas of the crystal with a Pt(100)- $(\sqrt{2} \times \sqrt{2})R45^\circ$ -S may not be detected in the presence of a Pt(100)-(2x2)-Cu/S using a kinematic analysis of the patterns. If the surface is assumed to have taken solely these two surface structures with the Pt(100)- $(\sqrt{2} \times \sqrt{2})R45^\circ$ -S forming on the Pt(100) where the crystal was not covered by copper islands, the copper island area may be determined. If 'P' is the proportion of the crystal face covered with copper and exhibiting the Pt(100)-(2x2)-Cu/S structure with local coverage 0.25 the uncovered platinum with sulphur coverage 0.5 make up "1-P" of the surface.

The ratio of the Auger signal from the sulphur covered platinum surface to that of the surface made up of copper islands of fractional area P is then

$$\frac{2}{P + 2(1-P)} \quad \text{measured as } 1.58$$

From this the proportion P of the crystal covered by copper was 0.73. The copper deposition in this case was 1.2 M-L. This was in good agreement with Seah's estimate⁽¹⁴⁸⁾

of 0.5 M-L discrepancy between the coverage of a given layer during deposition calculated assuming perfect monolayer growth and that resulting from the random arrival of the evaporant.

Similarly, for the 0.55 M-L deposition of copper on platinum the value of P was then

$$\frac{2}{P + 2(1-P)} = \frac{147}{111}$$

$$\therefore P = 0.49$$

In this case the discrepancy between calculated and measured coverage had dropped, indicating the convergence to zero error at the uncovered clean surface. (see also Figure IV.3)

The Pt(100)-(2x2) may be made up by the superposition of Pt(100)-($\sqrt{2} \times \sqrt{2}$)R45° and 2 domains of Pt(100)-(2x1). This latter structure was reported by Domange and Oudar⁽⁸²⁾ for sulphur growth on Cu(100) before the development of bulk sulphides. As this corresponded to a surface coverage of 0.5 the total sulphur coverage of clean or copper covered platinum would have been identical. The sulphur Auger signals in each case would have differed only by the effect of the change in backscatter current due to the single or sub-monolayer copper. The mean free path for the incident electrons at 2.5 keV is ~30 Å in the crystal resulting in small backscatter contribution from the first layer (~6%).

The sulphur treatment was not continued to the very high exposures (>1000 L) used by Domange and Oudar because of the experimental difficulty arising from gun filament poisoning. The Pt(100)-(2x2)-Cu/S may have been a stage

which appeared before the development of the Pt(100)-(2x1) and bulk sulphides. However in this work the Auger signal during exposure appeared to have reached a plateau when the initial patterns were observed to be strong.

IV.7 The Surface Structure of Evaporated Gold.

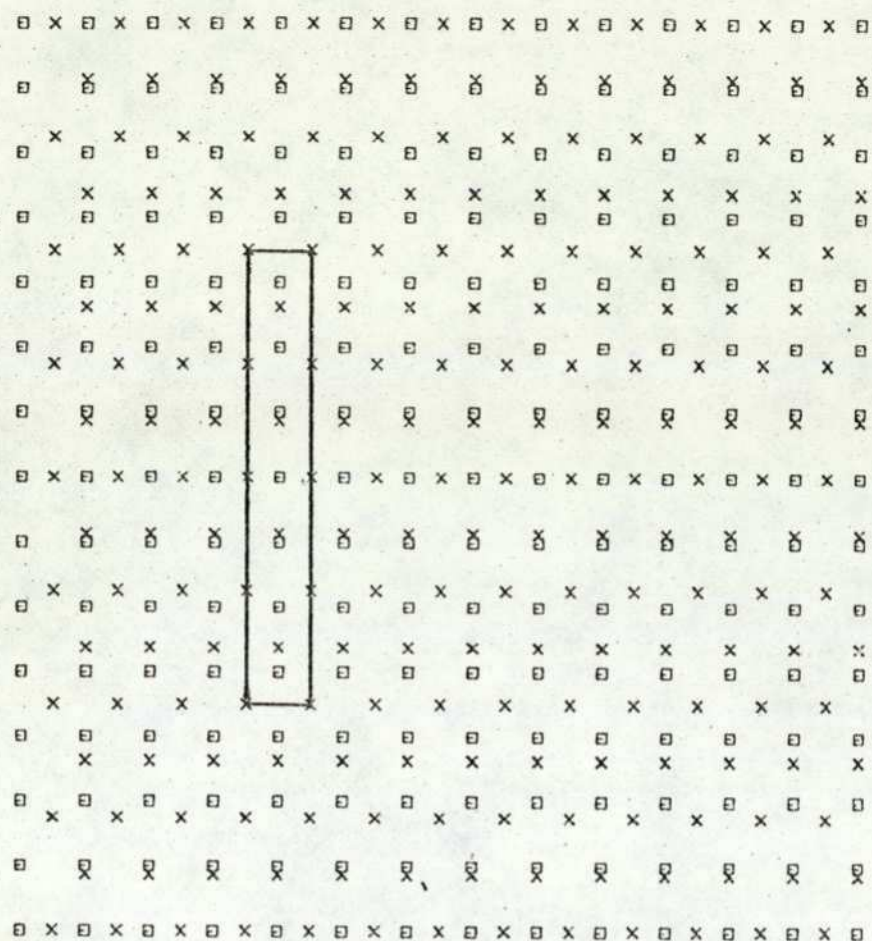
The results obtained here show an interesting variation on the normal Au(100) apparently clean surface pattern. This (7x1) structure has been observed for thin gold films deposited on sodium chloride. The Pt(100)-(7x1)-Au pattern may be explained as a reorientation from Au(100) to Au(111) at the surface. As the pattern showed no splitting of fractional order spots, unlike the Pt(100)-(5x1), the coincidence occurred at a true (7x1) mesh.

If the initial gold deposition took up the platinum substrate spacing, as was observed for copper films, the coincidence was between an Au(111) layer of interatomic spacing 2.884 Å and the Pt(100) spacing. The compression required to maintain the gold in registration with the platinum along one axis was 4%. The inter-row spacing of the hexagonal layer in the $\langle 10 \rangle$ direction for undistorted Au(111) planes is 2.497 Å. The approach to coincidence is shown in Table IV.2. The minimum distortion from the gold spacing would occur if the 10th row of the Au(111) layer contracted by 0.02% to coincide with the 9th row of the Pt(100). The resultant coincidence pattern would then be Pt(100)-(9x1). If slight contraction occurred in both axes

Au(111)		Pt(100)		Au(100)	
Row	Inter-row spacing	Row	Inter-row spacing	Row	Inter-row spacing
1	2.497	1	2.774	1	2.884
2	4.995	2	5.548	2	5.768
3	7.492	3	8.322	3	8.652
4	9.990	4	11.096	4	11.536
5	12.487	5	13.870	4	11.536
6	14.984	5	13.870	5	14.420
7	17.482	6	16.644	6	17.304
8	19.979	7	19.418	7	20.188
9	22.476	8	22.192	8	23.072
10	24.970	9	24.966	9	25.956
11	27.467	10	27.740	10	28.840

Au(111)		Pt(100)		Distortion		Au(100)		Distortion	
Row		Row	Mismatch %	to fit %		Row	Mismatch %	to fit %	
1		1	-10.0	+11.0		1	-13.4	+15.5	
2		2	-19.9	+11.0		2	-26.8	+15.5	
3		3	-29.9	+11.0		3	-40.2	+15.5	
4		4	-39.9	+11.0		4	-53.6	+15.5	
5		5	-49.9	+11.0		4	+33.0	- 7.6	
6		5	+40.2	- 7.4		5	+19.6	- 3.8	
7		6	+30.2	- 4.8		6	+ 6.2	- 1.0	
8		7	+20.2	- 2.8		7	- 7.2	+ 1.0	
9		8	+10.2	- 1.3		8	-		
10		9	+ 0.1	-0.02					
11		10	- 9.8	+ 1.0					

TABLE IV.2 The inter-row spacings of Au(111), Pt(100), and Au(100) showing probable coincidences.



□ Substrate Mesh Pt(100)

$$a = 2.774 \text{ \AA} \quad b = 2.774 \text{ \AA} \quad \gamma = 90^\circ$$

× Overlayer Mesh Au(111)

$$a = 2.796 \text{ \AA} \quad b = 2.774 \text{ \AA} \quad \gamma = 119.74^\circ$$

FIGURE IV.5 A possible mechanism for the formation of the Pt(100) (7x1)-Au.

the next coincidence condition would be the 8th row of the Au(111) aligning with the 7th row of the Pt(100) as shown in Figure IV.5. The contraction in the $\langle \bar{1}, 2 \rangle$ direction was 3.9% and in the $\langle \bar{2}, 1 \rangle$ direction was 3.1% with the interrow angle of 120° modified to 119.74° .

Table IV.2 also shows the required distortions to fit the Au(111) mesh on the Au(100) mesh. The compressions occurring in each (100) axis in this case is 0% and 3.8% when the 6th row of (111) mesh registers with the 5th row of the (100) mesh i.e. Au(100)-(5x1). Compression in the $\langle 01 \rangle$ direction of the substrate by 4.8% would result in the Au(100)-(5x20) pattern.

The difference between the Pt/Au(100)-(7x1) and Au(100)-(5x20) pattern is consistent with pseudomorphic growth of the initial gold layers with the Pt(100) substrate. No evidence was obtained to indicate the degree of intermixing of the two metals.

CHAPTER V CONCLUSIONS AND THEIR SIGNIFICANCE TO RELATED WORK.

The general conclusions to be drawn from the results detailed above are described here with their significance to continuing work in other laboratories.

V.1 The Pt(100)-(5x1) Surface Structure.

This structure is associated with surface layer reorientation from the bulk single crystal (100) mesh to partial coverage by a Pt(111) mesh. It was obtained by standard cleaning, particularly high temperature oxidation, to reduce impurity levels below the detection limits of A.E.S. It could also coexist with LEED patterns and Auger spectra indicating surface carbon. Calcium, which had been thought to be present near the surface of the (5x1) structure, was detected on all three low index crystal faces of platinum on annealing after severe oxygen treatment. It could not be correlated directly with the presence of the (5x1) LEED pattern.

The Pt(100)-(5x1) structure is important in a reorientation theory of catalysis. Any dependence on low concentrations of particular impurities must be determined to enable the theory to be tested against a catalytic system in which a reaction should benefit from the conversion of (100) faces of platinum crystallites to (111) faces. The electron beam used to detect the impurities at the surface may cause local loss of the impurity before detection. This may be overcome by rapid Auger analysis or by the use of X-ray P.E.S.

Work with this latter method should employ an X-ray source of energy just above the ionisation energy of the material suspected to increase the inherently low sensitivity of the method.

An impurity near to the Pt(100) surface would help to explain (100)→(111) surface transition but has yet to be identified conclusively.

V.2 Quantitative A.E.S.

This work demonstrates that it is possible to carry out quantitative analysis of the first few atomic layers of a specific simple alloy system. The copper Auger electron signals were dependent not only on the mass of copper at the surface but also on the structure of the deposits and on the presence of impurities. No significant changes in the copper LMM Auger peak shapes were detected between cleaned and oxygen treated copper films on Pt(100) to account for observed changes in peak sizes. The structural effects would be clarified in a comparison between spectra from several low index faces of bulk copper crystals and also the particular structures observed here.

If the quantitative use of A.E.S. is to be extended to more complex alloy and impurity measurement than the simple cases described here the effect of the local atomic environment on each element in a matrix must be determined. This may be achieved by investigating the Auger response from impurity or alloying components in a matrix during controlled deposition of further matrix material.

The enhancement or attenuation of the signal from single atoms or groups of atoms buried in a matrix may then be determined. The amount of data required to generalise the quantitative use of A.E.S. in alloy systems demands rapid data acquisition techniques. An extension of Seah's method of multiple evaporation sources would enable many metals to be studied rapidly.

The depth of impurity atoms below a surface may be determined if two transitions resulting in Auger electrons with different, known inelastic mean free paths in the surrounding matrix can be detected to fix the position by their different rates of signal attenuation.

V.3 Pseudomorphic Growth

Pseudomorphic growth was found to occur for up to 5 monolayers of copper deposited on Pt(100) at $\sim 20^{\circ}\text{C}$. The LEED pattern exhibited by these surfaces was a Pt(100)-(1x1)-Cu. The gas adsorption on this surface was found to be very different from that on Pt(100) but similar to that on a bulk copper crystal cut to expose Cu(100). This is of relevance to a consideration of replica catalyst systems. If the geometry of a Pt(100) crystal face is the sole parameter in the success of a catalyst any method of replication of the geometry should also succeed. This result indicates that gas adsorption is primarily influenced by the surface electronic effects.

V.4 Gas Adsorption on Alloy Films

After the adsorption of H_2S had been found by LEED to form different structures on the Pt(100) surface to that on the copper film surface it was possible to determine the surface fractional coverage by copper islands. This confirmation of a static adatom copper film growth mechanism was in agreement with the calibrated deposition results and effects of annealing the low temperature ($20^{\circ}C$) deposited films.

This technique should be applicable to the analysis of any system in which two surface structures are present and which adsorb a third species differentially. This adsorption may then be quantified by A.E.S. which gives a signal proportional to surface coverage up to the first monolayer. The areas of different phases at an alloy surface may be determined in this way.

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